PB81-224289

Materials Balance for Dyes and Pigments from Benzidine and Three Benzidine Derivatives

Midwest Research Inst.
Kansas City, MO

Prepared for

Environmental Protection Agency
Washington, DC

May 81

U.S. Department of Commerce
National Technical Information Service
NTIS

50272-101

REPORT DOCUMENTATION PAGE

1. REPORT NO. EPA-560/2-81-001

2.

3. Recipient's Accession No. PB81 224289

4. Title and Subtitle
Materials Balance for Dyes and Pigments from Benzidine and Three Benzidine Derivatives

5. Report Date May 1981

6.

7. Author(s) Thomas W. Lapp, Thomas L. Ferguson, Howard Gadberry, Fritz Hoffmeister, Fred Hopkins

8. Performing Organization Rept. No.

9. Performing Organization Name and Address
Midwest Research Institute
425 Volker Boulevard
Kansas City, Missouri 64110

10. Project/Task/Work Unit No. Task V

11. Contract(C) ~~or Grant(G)~~ No.
(C) 68-01-3896
(G)

12. Sponsoring Organization Name and Address
Environmental Protection Agency
Office of Pesticides and Toxic Substances
Washington, D.C. 20460

13. Type of Report & Period Covered Final Report

14.

15. Supplementary Notes
Roman Kuchkuda, Project Officer

16. Abstract (Limit: 200 words)

The processes for and losses resulting from the manufacture of dyes and pigments are presented. Consumption profiles and estimated losses are summarized for bis-azobiphenyl (BAB) dyes in the textile, leather, and paper industries and for pigments in the rubber, plastics, printing ink, textile printing, and coatings industries. During dye production, losses occur in by-products, process venting, process losses, product filtration, and transfer and handling of solid dyes. For 1978, about 80% of the total BAB dye use in the testile, paper, and leather industries was incorporated into the final product and 20% was lost to solid waste or wastewater. Losses in wastewater were about 50% greater than in solid waste. During pigment production, losses result from soluble by-products and handling and transfer losses. In 1978, estimated total losses due to handling and transfer of pigments during production were 190,000 to 558,000 lb. The printing ink industry consumed the majority of the total pigment production. In 1978, about 75% of the total pigment used in the five industries was incorporated into the final product and 25% was lost to wastewater or solid waste. Essentially all of the pigment loss was as solid waste with very small quantities in wastewater.

17. Document Analysis a. Descriptors

Benzidine
Dichlorobenzidine
Dimethylbenzidine
o-Tolidine
Dimethoxybenzidine
Dianisidine
Materials Balance
Direct Dyes
Diarylide Pigments
Production
Exposure
Solid Waste
Industrial Waste
Water Pollution

b. Identifiers/Open-Ended Terms
Materials Balance
Solid Wastes

c. COSATI Field/Group

18. Availability Statement
Unlimited Distribution

19. Security Class (This Report) UNCLASSIFIED

20. Security Class (This Page) UNCLASSIFIED

21. No. of Pages 213

22. Price

OPTIONAL FORM 272 (4-77)

PB81-224289

United States
Environmental Protection
Agency

Office of
Toxic Substances
Washington DC 20460

EPA-560/2-81-001
May 1981

Toxic Substances

EPA

Materials Balance for Dyes and Pigments from Benzidine and Three Benzidine Derivatives

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA 22161

This document is available through the National Technical Information Service (NTIS), Springfield, Virginia 22161, Telephone No. (703) 557-4650.

CHEMICAL TECHNOLOGY AND ECONOMICS IN ENVIRONMENTAL PERSPECTIVE

Task V - Materials Balance for Dyes and Pigments from Benzidine and Three Benzidine Derivatives

FINAL REPORT
May 1981

EPA Contract No. 68-01-3896

For

Environmental Protection Agency
Office of Toxic Substances
401 M Street, S.W.
Washington, D.C. 20460

Attn: Mr. Roman Kuchkuda
Project Officer

DISCLAIMER

This report has been reviewed by the Office of Toxic Substances, U.S. Environmental Protection Agency, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the U.S. Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

PREFACE

This report presents results of a materials balance for dyes and/or pigments produced from benzidine, 3,3'-dimethylbenzidine, 3,3'-dimethoxybenzidine, and 3,3'-dichlorobenzidine during the period 1975 through 1978.

This study was performed by Midwest Research Institute as Task V under Contract No. 68-01-3896 for the Office of Toxic Substances of the U.S. Environmental Protection Agency. Project officer for this study was Mr. Roman Kuchkuda. Principal Midwest Research Institute contributors to this study included: Dr. Thomas W. Lapp (Task Leader), Mr. Thomas L. Ferguson, Mr. Howard Gadberry, Mr. Fritz Hoffmeister, Mr. Fred Hopkins, and Mr. Brian Thompson. This contract is being performed under the supervision of Dr. Edward W. Lawless, Head, Technology Assessment Section.

MRI would like to express a special note of appreciation to the technical advisor for this task, Ms. Elizabeth Bryan, Office of Pesticides and Toxic Substances, for the assistance and encouragement provided during the course of this study.

Midwest Research Institute would also like to express sincere appreciation to the many industry sources who provided technical input to this study.

Approved for:

MIDWEST RESEARCH INSTITUTE

Bruce W Macy

Bruce W. Macy Director
Center for Technoeconomic Analysis

CONTENTS

Preface. iii

1. Introduction 1-1
2. Summary. 2-1
    Dye production and use. 2-1
    Pigment production and use. 2-9
    Miscellaneous uses. 2-16
    Preliminary materials balance 2-18
3. Dye Production 3-1
    Production processes. 3-1
    Sources of losses during dye production 3-3
    Production of BAB dyes. 3-6
    Imports and total benzenoid dye consumption 3-7
    Materials balance for dye production. 3-23
    Dye usage 3-30
4. Textile Dyeing 4-1
    Industry characterization 4-1
    Textile dyeing and dyestuff printing. 4-4
    Estimated consumption 4-6
    Estimated losses. 4-8
5. Leather Tanning Industry 5-1
    Industry overview 5-1
    Leather tanning and dyeing processes. 5-3
    Dye consumption 5-5
    Estimated losses. 5-7
6. Paper Industry 6-1
    Industry overview 6-1
    Paper processing and dyeing 6-5
    Dye consumption 6-9
    Estimated losses. 6-10
7. Pigment Production 7-1
    Manufacturing process 7-1
    Production history. 7-7
    Estimated losses. 7-14
    Pigment usage 7-19
8. Plastics and Rubber Industry 8-1
    Industry overview - plastics. 8-1
    Pigment consumption - plastics. 8-6
    Estimated losses - plastics 8-8
    Industry overview - rubber industry 8-14
    Rubber production process 8-16
    Pigment consumption - rubber. 8-18
    Estimated losses - rubber 8-18

Preceding page blank

CONTENTS (continued)

9. Printing Inks. 9-1
    Industry characteristics. 9-1
    Ink production by types 9-3
    Manufacture of printing inks. 9-5
    Source of production loss 9-7
    Waste handling and treatment. 9-11
    Estimated losses. 9-14
    Ink losses in printing. 9-14
    Postprinting disposition. 9-18
10. Paint and Coatings Industry. 10-1
    Industry characteristics. 10-1
    Paint manufacturing 10-1
    Pigment usage 10-5
    Estimated losses in paint manufacture 10-9
    Losses in paint application 10-15
11. Textile Printing 11-1
    Industry characterization 11-1
    Printing processes. 11-1
    Estimated pigment consumption 11-5
    Pigment losses. 11-6
12. Miscellaneous Uses 12-1
    Laboratory and test applications. 12-1
    Home use dyes 12-2
    Arts and craft dyes 12-4
    Marking instruments 12-4
    Other BAB dye uses. 12-6
13. Preliminary Materials Balance. 13-1
    BAB dyes. 13-1
    Pigments. 13-4
    Overall perspective 13-4

References R-1

Appendix

A. Report Reviewers A-1
B. Sample Calculations. B-1

FIGURES

Number		Page
3-1	Example of BAB dye manufacturing process	3-4
3-2	Characteristics of BAB dye production industry	3-13
3-3	Trends in BAB dye production	3-22
3-4	Materials balance for BAMB raw materials in dye manufacturing.	3-25
4-1	Typical textile dyeing process	4-5
5-1	A general process flow diagram illustrating tannery inputs and wastestreams.	5-11
6-1	Simplified representation of a beater.	6-6
6-2	Simplified representation of a conical continuous refiner.	6-7
6-3	A general process flow diagram illustrating papermaking inputs and wastestreams.	6-13
7-1	General flow diagram for pigment manufacture	7-3
9-1	Sample materials balance for diarylide pigments in printing inks in 1978.	9-15
10-1	Flow diagram of solvent base paint manufacturing process .	10-4
10-2	Flow diagram of water base paint manufacturing process . .	10-6
11-1	Typical printing process	11-3

TABLES

Number Page

2-1 Estimated Quantities of BAB Dye Consumed in the United States. 2-3

2-2 BAB Dye Losses from Production Processes 2-4

2-3 Approximate Percent BAB Dye Consumption by Area. 2-5

2-4 Estimated Materials Balance for BAB Dyes by Use Area . . . 2-19

2-5 Estimated Materials Balance for 3,3'-Dichlorobenzidine, 3,3'-Dimethylbenzidine, and 3,3'-Dimethoxybenzidine Based Pigments in Use Areas. 2-20

3-1 BAB Dyes on the U.S. Market in 1979. 3-8

3-2 Code Letters of Manufacturers, Importers, and Distributors 3-12

3-3 U.S. Production, Import, and Sales Data for Commercial BAB Dyes (in lb), 1975 to 1978 3-14

3-4 Estimated Quantities of BAB Dye Consumed in the United States. 3-24

3-5 BAB Dye Losses from Production Processes 3-26

3-6 Basis for Materials Balance Calculations 3-27

3-7 Unreacted BAMB Raw Material in Dye Manufacture 3-29

3-8 Estimated Active Dye Consumption in the U.S. During 1975-1978. 3-30

3-9 Approximate Percent BAB Dye Consumption by Area. 3-31

4-1 Estimated U.S. Dyed Fabric Production (10^6 lb) of Fabric . 4-3

4-2 Apparatus Used in Textile Dyeing 4-7

4-3 Estimated Bisazobiphenyl Dye Consumption in the Textile Industry 4-8

TABLES (continued)

Number Page

4-4 Estimated Bisazobiphenyl Dye Losses in Textiles. 4-9

4-5 Fiber Losses During Finishing and Other Processing Steps . 4-11

4-6 Estimated Bisazobiphenyl Dye Loss in the Textile Industry. 4-12

5-1 A Partial Listing of the Categories and Types of Leather Produced by U.S. Tanners 5-2

5-2 BAB Dyes Used in Leather Tanning, 1975-1978. 5-6

5-3 Estimated Consumption of BAB Dyes in the Leather Industry. 5-7

5-4 Overall Dye Consumption in the Leather Industry (1975-1978). 5-8

5-5 Approximate Consumption of BAB Dye by the Leather Industry (1975-1978) 5-9

5-6 Estimated Losses of Bisazobiphenyl Dyes in the Leather Industry 5-12

6-1 Origin and Use of Various Wood Pulp. 6-2

6-2 Paper Production by End Use, 1975-1978 6-3

6-3 Commercial Dye Usage in Paper and Paperboard 6-9

6-4 Estimated Consumption of BAB Dyes by the Paper Industry. . 6-11

6-5 Summary of Estimated Bisazobiphenyl Dye Losses from the Paper Industry 6-12

7-1 Structures of Selected Diarylide Pigments. 7-5

7-2 Pigment Manufacturers, 1975-1978 7-8

7-3 U.S. Production and Imports of Selected Pigments 7-12

7-4 Estimated Losses of 3,3'-Dichlorobenzidine, 3,3'-Dimethylbenzidine, and 3,3'-Dimethoxybenzidine During their Manufacture. 7-15

TABLES (continued)

Number		Page
7-5	Estimated Losses of 3,3'-Dichlorobenzidine, 3,3'-Dimethylbenzidine, and 3,3'-Dimethoxybenzidine During Pigment Production	7-16
7-6	Estimated Pigment Losses Due to Transfer and Handling at Production Facilities, Quantity (1,000 lb)	7-18
7-7	Consumption of Pigment by Use Area	7-19
8-1	Production of Selected Resins, 1975-1978	8-2
8-2	Estimated Consumption of Pigments in the Plastics Industry	8-7
8-3	Estimated Amount of Pigments Consumed by Resin (1975) (Quantity in 1,000 lb)	8-9
8-4	Estimated Amount of Pigment Consumed by Resin (1976) (Quantity in 1,000 lb)	8-10
8-5	Estimated Amount of Pigments Consumed by Resin (1977) (Quantity in 1,000 lb)	8-11
8-6	Estimated Amount of Pigments Consumed by Resin (1978) (Quantity in 1,000 lb)	8-12
8-7	Estimated Pigment Loss in Resin Compounding Stage	8-13
8-8	Estimated Pigment Losses Vis Resin Processing	8-14
8-9	Standard Industrial Classification (SIC) Codes for Rubber and Miscellaneous Plastic Products	8-15
8-10	U.S. Rubber Production by Type, 1975-1978	8-17
8-11	Consumption of Pigments - Rubber Industry	8-18
8-12	Estimated Pigment Loss in the Rubber Industry	8-19
9-1	1976 Production Volume in Pounds	9-2
9-2	1977 Ink Shipments by Type of Ink	9-2

TABLES (continued)

Number Page

9-3 Distribution by Printing Process 9-3

9-4 Estimated Diarylide Pigment Consumption in Printing Inks . 9-6

9-5 Wastewater Pretreatment Prior to Discharge 9-11

9-6 Analytical Data from Individual Plant Sites (Selected Compounds Only). 9-13

9-7 Estimated Losses from the Printing Ink Industry. 9-16

9-8 Estimated Fate of Diarylide Pigments in Printed Material . 9-19

10-1 Distribution of Large Paint Plants, by State 10-2

10-2 Dairylide Pigments in Paint Production 10-7

10-3 Estimated Dairylide Pigment Consumption in Paints. 10-8

10-4 Relative Usage of Color Pigments by Paint Plants 10-10

10-5 Methods of Tank Cleaning 10-12

10-6 Volume of Wastewater Generated by Paint Plants 10-13

10-7 Estimated Pigment Loss from Paint Manufacturing - 1978 . . 10-14

10-8 Estimated Pigment Loss from Paint Manufacture. 10-15

10-9 Estimated Pigment Loss from Paint Application. 10-17

11-1 Estimated Quantity of Fabric Printed by Process (1975-1978). 11-2

11-2 Estimated Dairylide Pigment Consumption in Textile Printing 11-5

11-3 Estimated Dye and Pigment Losses in the Textile Printing Process. 11-7

11-4 Estimated Dairylide Pigment Loss in Textile Printing . . . 11-8

TABLES (concluded)

Number		Page
12-1	Estimated Losses from Home Dyes.	12-3
12-2	Estimated Losses from Crayon Production.	12-5
13-1	BAB Dye Losses From Production Processes	13-2
13-2	Estimated Materials Balance for BAB Dyes by Use Area . . .	13-3
13-3	Estimated Losses of Raw Material During Manufacture and Pigment Production	13-5
13-4	Estimated Pigment Loss in Production Process	13-6
13-5	Estimated Materials Balance for 3,3'-Dichlorobenzidine, 3,3'-Dimethylbenzidine and 3,3'-Dimethoxybenzidine Based Pigments in Use Areas.	13-7

SECTION 1

INTRODUCTION

Benzidine and three of its congeners,* 3,3'-dichlorobenzidine (DCB), 3,3'-dimethoxybenzidine (o-dianisidine, DMOB), and 3,3'-dimethylbenzidine (o-tolidine, DMB), are important starting materials for the production of a variety of dyes or pigments. Benzidine is used solely for the production of dyes and DCB is currently used solely for the manufacture of pigments. The other two congeners, DMB and DMOB, are used in the production of dyes and pigments. These dyes and pigments are widely used and thus these may have potential for widespread environmental exposure. Benzidine has been recognized for some time as a human carcinogen. Laboratory experiments suggest that the other three starting materials may also be carcinogenic to laboratory animals. In addition, the National Cancer Institute (NCI) recently recommended that three dyes based on benzidine be handled in the workplace as if they were human carcinogens.

This study was undertaken as the first step in the evaluation of the potential for environmental exposure due to these compounds. The overall objective was to develop a preliminary materials balance for the production and use of pigments or dyes based on benzidine, 3,3'-dimethylbenzidine, 3,3'-dichlorobenzidine, and 3,3'-dimethoxybenzidine.

The specific dyes and pigments considered in this report were selected by the Environmental Protection Agency (EPA). The specific objective was to compile, to the extent possible, a complete materials balance utilizing available data from trade publications, government reports, and industry sources. In those instances where data were unavailable, Midwest Research Institute (MRI) was to estimate quantities.

---

* In commercial practice, these three congeners are not produced from benzidine per se, but are synthesized from other chemical precursors.

Considerable information was obtained from industry sources who wished to remain anonymous; MRI has attempted to abide by these wishes whenever possible. As a result, industry sources are cited throughout the report, but no specific references are provided.

During the course of this study, numerous areas were found for which data were unavailable, and estimates were made based on the best available information. Because a large portion of the data presented in this report is based on estimated quantities, the results of this materials balance should be considered preliminary until more definitive data are available.

Throughout this report, reference will be made to "benzidine based" dyes. This terminology refers specifically to those dyes based on benzidine. Similarly, dyes based specifically on 3,3'-dimethylbenzidine and 3,3'-dimethoxybenzidine will be referred to as 3,3'-dimethylbenzidine based and 3,3'-dimethoxybenzidine based, respectively. The term "bisazobiphenyl" (BAB)-dyes is employed where a more general term is required to include all dyes based on benzidine, 3,3'-dimethylbenzidine, and 3,3'-dimethoxybenzidine. The term "bisaminobiphenyl" (BAMB) starting material is used when referring to benzidine, 3,3'-dimethylbenzidine, and 3,3'-dimethoxybenzidine collectively as the starting material for dyes.

This report has been reviewed by numerous organizations and companies directly related to dyes and pigments. A listing of those who received copies of the draft final report (dated August 31, 1979) for review is presented in Appendix A. This report reflects those review comments which were deemed to have merit.

SECTION 2

SUMMARY

A summary of the results of this preliminary materials balance study is presented in this section. The processes for and losses resulting from the manufacture of dyes and pigments are included. Consumption profiles and estimated losses are summarized for bisazobiphenyl (BAB) dyes in the textile, leather, and paper industries and for pigments in the rubber and plastics, printing ink, textile printing, and paint and coatings industries. A summation of the materials balance for the period 1975 through 1978 is presented.

DYE PRODUCTION AND USE

Information is presented for the production of BAB dyes and usage of these dyes by various industries. Losses occurring during the manufacture and use have been derived from known or estimated data.

Dye Production

A number of commercial dyes are being produced in the United States from three bisaminobiphenyl (BAMB) precursors: benzidine, 3,3'-dimethylbenzidine, and 3,3'-dimethoxybenzidine. The production processes for these BAB dyes involve a complex series of batch processes carried out over a range of pHs, temperatures, and reaction times. Actual yield of saleable dye at the end of the manufacturing process ranges from ~ 76 to ~ 93% based on the starting BAMB raw material and depending on the particular dye and production process involved. However, because of the complexity of the production processes, even small operating problems or the lack of operator attention can result in a reduction in product yield of 10% or more.

The losses of BAMB based materials during dye production processes, i.e., conversion to unwanted by-products or removal from the process stream had not previously been well quantified. However, the following sources of losses have been identified, and losses have been estimated.

* By-Products - Loss of BAMB raw material from the production of unwanted by-products or degradation products during the production process. By-product losses typically range from 5 to 15%.

* Process Vent - Loss of material to the process vent system, estimated to be $\leq$ 0.1% of the original BAMB raw material, in the form of original BAMB raw material, active dyes, and by-products.

* Process Losses - Loss of BAMB based material resulting from pumping losses, spills, leaks, and intermediate purification steps in the production process. These losses are estimated to be from practically zero (0.25%) to 1%.

* Product Filtration Losses of dye during the filtration of the crude dye product (suspension) estimated to be 1 to 3%.

* Drying, Grinding, Standardizing, and Packaging - Losses in these final steps are estimated to be 1 to 5% as active dye.

* Raw Materials Carryover - Traces of unreacted BAMB raw materials in the finished dye product. Dyes are usually stated to contain ≦ 10 ppm of the benzidine. It was assumed that this level applies to all three BAMB raw materials.

Data on U.S. production, imports, and sales of standardized commercial BAB based dyes for 1975 through 1978 have been tabulated. These data are based on data published by the U.S. International Trade Commission and information obtained from confidential industrial sources. The data from these sources have been supplemented and modified where needed by Midwest Research Institute (MRI) estimates. These data are presented in Table 2-1.

Estimates were then made of the overall materials balance for the three BAB dyes during their production processes. These estimates were based on the sources and levels of loss identified, the production rates given, and other specific assumptions. Table 2-2 presents a summary of this balance.

Estimates of dye consumption data were developed for the various use areas based on information obtained from industry sources. Most of these sources agreed that the percentage consumption of dyes based on 3,3'-dimethoxybenzidine and 3,3'-dimethylbenzidine had remained relatively constant from 1975 through 1978. Large changes, however, had occurred for the benzidine based dyes. A summary of BAB dye consumption by major use area is given in Table 2-3.

Textile Dyeing

The principal BAB dye consumption occurs in textile mill products where fibers are received and prepared for transformation into yarn, thread, or webbing. Other processes include converting the yarn or web into fabric or similar products and finishing of the material. Except for losses of material as scrap when patterns are cut, no dye loss occurs in the apparel industry. Dyes of interest to this study are used primarily with cellulosic or cotton materials; minor use areas include polyester/cotton and nylon/cotton blends.

The same general dyeing process is employed for all the dyes of interest with minor variations due to differences in the particular dye used, the form of the fiber, and the type of fiber. A typical dyeing process would include the following steps:

TABLE 2-1. ESTIMATED QUANTITIES OF BAB DYE CONSUMED IN THE UNITED STATES

Type of Dye	Source	Quantity (10^6 lb)[a] 1975	1976	1977	1978
Benzidine	U.S. production[b]	3.8-4.6	5.8-7.0	4.1-4.5[c]	1.5-1.7
	Import	0.8-1.0	0.5-0.7	1.4-1.8	2.0-2.4
	Consumption	4.6-5.6	6.0-8.0[d]	5.3-6.5	3.4-4.2[e]
3,3'-Dimethoxybenzidine	U.S. production	1.6-2.0	2.2-2.6	1.4-1.8[c]	2.5-3.1[c]
	Import	0.1-0.2	0.1-0.2	0.1-0.2	0.2-0.4[c]
	Consumption	2.0-2.4	2.1-2.5	2.5-3.1[c]	3.5-4.3[f]
3,3'-Dimethylbenzidine	U.S. production[c]	0.62-0.76	0.66-0.80	0.63-0.77	0.74-0.90
	Import[c]	0.01-0.03	0.03-0.05	0.03-0.05	0.13-0.17
	Consumption[g]	0.75-0.91	0.75-0.91	0.63-0.77	0.74-0.90

---

[a] All quantities are in terms of standardized commercial dyes; they do not represent 100% dye. To convert to active dye content, see footnote (b), Table 3-6. Estimated error limits used to derive the consumption ranges were generally ± 10%.

[b] Data from Table 3-7.

[c] Data supplied by DETO (1980).

[d] Estimated by DETO (1980) to be 5.9; estimated by MRI to be 7.0 ± 1.0.

[e] Estimated by DETO (1980) to be 3.8.

[f] Stated by the U.S. International Trade Commission (letter from J. O. Parker to S. D. Jellinek, November 19, 1979) to be 3.925 million pounds for the U.S. production quantity in 1978; estimated by DETO to be 3.9 million pounds for the 1978 U.S. consumption levels, including imports.

[g] Includes approximately 340,000 lb of dye used in numerous areas exclusive of textiles, leather, or paper. Examples of these use areas are lubricant and gasoline dyes (DETO, 1980).

TABLE 2-2. BAB DYE LOSSES FROM PRODUCTION PROCESSES[a]

	Active Dye Loss (1,000 lb)											
	1975			1976			1977			1978		
Distribution	BEN[b]	DMB[c]	DMOB[d]	BEN	DMB	DMOB	BEN	DMB	DMOB	BEN	DMB	DMOB
Processing losses (0.21-0.95%)[e]	5-26	< 1-4	1-8	7-40	< 1-4	2-10	5-26	< 1-4	1-7	2-10	< 1-5	2-12
Filtration losses (1-3%)	23-84	4-13	6-24	35-130	4-14	9-32	25-82	4-14	6-22	9-31	4-16	10-38
Drying, grinding, standardization, and packaging losses (1-5%)	23-140	4-22	6-40	35-210	4-23	9-53	25-140	4-23	6-36	9-52	4-26	10-63

[a] Active dye basis; an overall product yield of 84% (BAMB raw material base) was assumed.

[b] BEN = benzidine-based dyes.

[c] DMB = dimethylbenzidine-based dyes.

[d] DMOB = dimethoxybenzidine-based dyes.

[e] For methods of calculation used in this table, see Appendix B, I.

- Weighing and mixing of dye solution
- Addition of dye solution to fiber
- Water rinse of dyed fiber
- Water extraction
- Fiber drying

TABLE 2-3. APPROXIMATE PERCENT BAB DYE CONSUMPTION BY AREA

	1975	1976	1977	1978
Benzidine based dyes:				
Textile	50 - 60	45 - 55	45 - 55	40 - 50
Leather	20 - 25	20 - 25	25 - 30	45 - 55
Paper	20 - 25	25 - 30	20 - 25	5
3,3'-Dimethoxybenzidine based dyes:				
Textile	38 - 42	38 - 42	33 - 37	33 - 37
Leather	7 - 13	7 - 13	7 - 13	7 - 13
Paper	44 - 46	44 - 46	49 - 51	45 - 55
Other	~5	~5	~5	~5
3,3'-Dimethylbenzidine based dyes:				
Textile	44 - 50	44 - 50	36 - 41	45 - 50
Leather	6 - 9	6 - 9	5 - 8	4 - 9
Paper	3 - 6	3 - 6	5 - 8	~5
Other	~41	~41	~41	~41

The complexity of the textile industry and the variability in annual consumption of specific dyes due to style changes in apparel design make estimation of the consumption of specific BAB dyes very difficult. As a result, dye consumption could be estimated by dye type (i.e., benzidine based, 3,3'-dimethylbenzidine based, or 3,3'-dimethoxybenzidine based). Estimated BAB dye consumption levels for 1975 through 1978 are as follows (quantities of 100% dye in million pounds):

Base	1975	1976	1977	1978
Benzidine	1.2-1.7	1.4-2.3	1.2-1.8	0.7-1.1
3,3'-Dimethylbenzidine	0.4-0.5	0.4-0.5	0.4-0.6	0.7-0.8
3,3'-Dimethoxybenzidine	~ 0.11-0.16	~ 0.11-0.16	~ 0.08-0.11	~ 0.11-0.16
Total	1.7-2.4	1.9-3.0	1.7-2.5	1.5-2.1

The losses of dye during textile processing are in the dust from mixing operations, residual dyes in shipping containers and mixing and holding containers, and liquid waste from the dyeing, rinsing, and water extraction procedures. Sources of BAB dye losses and the estimated magnitude of each source is as follows:

Dust from mixing	0.05-0.1%
Residual dye in containers	0.02-0.05%
Process wastewater Direct dyes	5-30%
Acid dyes	2-5%
Unrecycled dye from continuous units	2-10%
Solid waste from processing (subsequent to dyeing)	1.0-1.5%

A summary of the estimated BAB dye losses resulting from these sources is shown in the following compilation (quantities of 100% active dye are in 1,000 pounds):

	1975	1976	1977	1978
Dust	1-2	1-3	1-2	1-2
Residual dye	~ 1	~ 1	~ 1	~ 1
Unrecycled dye	32-230	36-290	32-240	26-190
Process wastewater	80-690	90-870	80-720	65-570
Solid waste processing	16-35	18-44	16-36	13-29
Total	130-958	146-1,208	130-999	106-792

Leather Industry

In the leather tanning industry, shoe leather is the largest single product, but a wide variety of other leather goods is also marketed. The specific types and quantities of dyes used for leather products varies widely from year to year due to trends in fashion and the multiplicity of current manufacturers. The primary raw material for leather is cattle hide; all other hides contribute less than 10% of the total hides processed.

Leather is typically dyed in a batch mode process. During the dyeing operation, the hides and dye solution are mixed, commonly by the rotation of the drum. Approximately 85% of all tanned hides are dyed.

The predominant colors used by leather tanners are black, brown, and other colors used with brown to produce various shades of brown. Specific

BAB dyes used in leather tanning are difficult to ascertain for any given year due to changes in demand for different colors in different products. Because of the difficulty in identifying specific dyes, estimates of the total annual consumption were made for the three types of BAB dyes (i.e., benzidine based, 3,3'-dimethylbenzidine based, and 3,3'-dimethoxybenzidine based). A summary of the estimated consumption is as follows (quantities of 100% dye in 1,000 lb):

Base	1975	1976	1977	1978
Benzidine	460-725	620-1,025	675-990	765-1,155
3,3'-Dimethyl-benzidine	22-41	22-41	16-30	14-40
3,3'-Dimethoxy-benzidine	49-104	49-117	63-143	84-195
Total	531-870	691-1,183	754-1,163	863-1,390

Approximately 85 to 90% of the dye utilized in leather dyeing is successfully joined to the leather. If allowances are made for trimmings, buffing losses, and other miscellaneous losses, the lower end of this range is reduced to 80%. No definitive information was found to provide a quantitative breakdown for the fate of waste dyestuff from leather tanneries. However, from the information that is available it is estimated that ~ 99.8% of the losses occur as solid waste, ~ 0.1% liquid waste, and ~ 0.1% aerosolized waste. The solid waste is estimated to be comprised of 60% from wastewater screenings and sludge; 35% from trimmings and shavings; 3% from floor sweepings; and 2% finishing wastes. A summary of the estimated solid, liquid, and aerosolized wastes in terms of 100% dye is presented below (quantities in 1,000 pounds):

	1975	1976	1977	1978
Solid waste (99.8%)	53-174	69-236	75-232	86-277
Liquid waste (~ 0.1%)	~ 0.1-0.2	~-0.1-0.2	~ 0.1-0.2	~ 0.1-0.3
Aerosol waste (~ 0.1%)	~ 0.1-0.2	~ 0.1-0.2	~ 0.1-0.2	~ 0.1-0.3
Total	53-174	69-236	75-232	86-278

Paper Industry

The paper industry (including the paperboard industry) is a very large diversified industry producing 10 general types or classifications of paper: newsprint, printing and writing, packaging, special industrial, tissue, containerboard, boxboard, building paper, insulating and hard pressed board, and wet machine board. In 1978, approximately 64 million tons of paper of these 10 types were produced.

Though the equipment may vary, over 90% of all colored paper is dyed in the same manner--prior to its aggregation into sheets and while in an aqueous bath. In one very common method, dyeing occurs in a beater used to fragment fiber bundles and shorten individual fibers in the pulp. The principal alternative method consists of two or three separate machines--a pulper, a continuous refiner, and occasionally a deflaker. In each of these systems, the dye may be added as a liquid solution or a dry powder.

Dye consumption in the paper and paperboard industry ranges from 0 to 5 lb/ton of paper for unbleached kraft products, white paper and tissue, and white paperboard to 60 to 80 lb/ton for full shade tissue paper and brightly colored glassine. No data were available concerning quantities of specific BAB dyes consumed in the paper industry; some industry estimates were available for consumption by dye type (i.e., benzidine-based, 3,3'-dimethylbenzidine-based, and 3,3'-dimethoxybenzidine-based). These estimated consumption quantities are summarized below in thousands of pounds of 100% dye:

	1975	1976	1977	1978
Benzidine	460-725	775-1,230	540-825	85-105
3,3'-Dimethoxybenzidine	308-368	300-414	441-550	540-825
3,3'-Dimethylbenzidine	11-27	11-27	16-30	18-22
Total	779-1,120	1,094-1,671	997-1,405	643-952

Industry sources stated that 90 to 98% of the dye utilization in the coloration of paper is successfully joined to the papermaking materials. In order to allow for losses of dyed furnish and size, trimmings, and other miscellanous losses during production, the range is lowered to 80 to 95%. The remaining 5 to 15% of the dye consumed in processing is discarded as waste; it is thought that the majority of the waste ultimately becomes solid waste either as wastewater sludge, trimmings, plant dust, or other miscellaneous residues. It is estimated that ~ 99.8% of the losses are incorporated into solid waste, ~ 0.1% in liquid waste, and ~ 0.1% as aerosolized (volatilized) waste. A summary of these estimated BAB dye losses (in 1,000 lb of 100% dye) for the paper industry is presented below for the period 1975 to 1978:

	1975	1976	1977	1978
Solid waste	39-168	55-250	50-210	32-142
Liquid waste	~ 0.1-0.2	0.1-0.3	0.1-0.2	~ 0.1-0.2
Volatile waste	~ 0.1-0.2	0.1-0.3	0.1-0.2	~ 0.1-0.2
Total	39-168	55-251	50-210	32-142

PIGMENT PRODUCTION AND USE

Information is presented for the production of pigments and usage of these pigments by various industries. Losses occurring during the manufacture and use have been derived from known or estimated data. For purposes of this study, the EPA selected the following pigments: Reds 38 and 41; Oranges 13, 15, 16, and 34; Yellows 12, 13, 14, 17, 55, and 83; and Blue 25.

Production Process

The production of pigments from 3,3'-dichlorobenzidine, 3,3'-dimethoxybenzidine, and 3,3'-dimethylbenzidine proceeds by a batch process using the acid salt (usually the dihydrochloride salt) as the starting material. Preparation of the dichlorobenzidine compound occurs by the reduction of *o*-nitrochlorobenzene to the corresponding hydrazo compound, followed by acid rearrangement to the 3,3'-dichlorobenzidine dihydrochloride. Estimated losses of the dichlorobenzidine during production were 0.5 to 1.0% in the "acid stream" from the purification process and 0.5 to 1.5% in the waste stream from filtration of the final product.

Pigment production occurs by treatment of the appropriate compound with nitrous acid (generated *in situ*) to form the corresponding tetrazonium chloride which is reacted with a coupler to yield the desired pigment. On occasion the tetrazonium solution may be filtered prior to addition of the coupler solution; however, as a rule, this filtration step is omitted. Following addition of the coupler solution and after pigment formation is complete, the insoluble pigment is filtered from solution to form the presscake. The three processing alternatives for the presscake are: (a) shipped as the presscake, (b) transfer to a flusher and mixing with an oleoresinous material to form a flushed color paste, and (c) drying, pulverizing, and shipment as a dry toner.

The estimated total domestic production and published imports of the pigments for the 4-year period were as follows:

	Estimated production	Imports
1975	10,293,000-10,443,000	124,820
1976	14,034,000-14,179,000	275,930
1977	15,446,000-15,701,000	64,100
1978	19,281,000-19,536,000	35,080

In addition to losses during production of the starting material (i.e., 3,3'-dichlorobenzidine dihydrochloride, etc.), losses of the starting material (also includes soluble by-products) during pigment manufacture are as follows:

Filtration of tetrazonium solution (optional)	0.1-0.3%
Unreacted tetrazonium chloride or soluble by-product	0.5-1.0%

Losses of pigment during subsequent handling and processing are estimated to be:

Flushed color: handling and transfer	1-3%
Dry toner: handling and transfer	1-3%
Dry toner: pulverizer cleaning (optional)	0.5-1%
Dry toner: blender cleaning (optional)	~ 1%
Presscake: handling and transfer	0.5-1%

The estimated overall pigment losses for flushed color or dry toner production are 1 to 3%. If the optional pigment losses are employed for dry toner production, the overall estimated loss is increased by ~ 1.5 to 2%. For presscake production, the estimated losses are 0.5 to 1%. Estimated total loss of 3,3'-dichlorobenzidine, 3,3'-dimethylbenzidine, and 3,3'-dimethoxybenzidine in the raw material manufacturing process and pigment production process are as follows (quantities in 1,000 pounds):

	1975	1976	1977	1978
3,3'-dichlorobenzidine	60-142	83-194	92-216	116-273
3,3'-dimethoxybenzidine	3-8	3-10	3-10	3-10
3,3'-dimethylbenzidine	0.3-0.7	0.3-0.7	0.3-0.6	0

Estimated total losses due to handling and transfer of finished pigments derived from each of the compounds are (quantities in 1,000 pounds):

	1975	1976	1977	1978
3,3'-dichlorobenzidine	91-274	126-380	137-410	177-537
3,3'-dimethoxybenzidine	6-19	7-21	6-20	6-20
3,3'-dimethylbenzidine	0.5-1	0.5-1	0.4-1	0

Pigment usage within various product areas was estimated based on information from industry sources and published reports. Five industries were identified as major consumers of these pigments: printing ink, plastics, coatings, textile printing, and rubber. Pigment usage in marking instruments was included in the miscellaneous category. In terms of total quantity of pigment consumed, the printing ink industry consumes the majority of the total production.

Plastics and Rubber

In 1978, total plastics sales were approximately 34 billion lb, and the vast majority of these plastics were tinted or colored. For the pigments of interest to this study, nine resins were identified as employing one or more of these pigments. These resins were ABS, nylon, polyester/alkyd, low density polyethylene (LDPE), high density polyethylene (HDPE), polypropylene, polystyrene, polyurethane, and polyvinyl chloride. The nine resins comprised 80% of the total plastics production in 1978; of this total production for the nine resins, ~ 80% was tinted or colored.

The pigments employed in plastics were Reds 38 and 41, Oranges 13 and 16, and Yellows 13, 14, 17, 55, and 83. Yellows 14, 17, and 83 were consumed in quantities greater than 200,000 lb in 1978. Red 38 and Orange 16 were used at levels of approximately 140,000 to 160,000 lb. For all other pigments, estimated consumption was less than 100,000 lb in 1978. Estimated consumption figures for each pigment are also presented for 1975 through 1977.

Mixing and compounding are the principal stages in plastic production during which additives, such as pigments, plasticizers, or heat stabilizers, are incorporated into the resin. The pigments may be added to the resin in basically two forms: dry pigment or color concentrate. Dry pigment is added directly to a resin during the additive blending process. In a color concentrate, the pigment is predispersed in a medium such as the resin itself at levels of 35 to 50% pigment.

The majority of pigment losses are associated with the ultimate disposal of the consumer product. Few data were available from the plastics industry concerning losses of colorants in the resin compounding stage, but estimates were obtained of losses during fabrication of the final product. Sources of losses and the estimated magnitude of each loss are summarized as follows:

Handling and transfer of colorants and concentrates during compounding	1-2%
Waste plastic during processing -	
- thermoplastics	5-15%
- thermosets	10-30%

For each resin type, estimated losses were derived for thermoplastics and thermosets. Of the nine resins, seven were thermoplastics and two were thermosets. For all nine resins, the estimated total pigment losses during compounding and processing are as follows: 1975, 50,000-153,000 lb; 1976, 70,000-207,000 lb; 1977, 75,000-227,100 lb; and 1978, 82,000-247,000 lb.

In the rubber industry, potential use areas for these pigments are rubber and plastic footwear, rubber and plastic hoses and belts, and other fabricated rubber products. Very little information was obtained from industry concerning the percent of rubber colored by the diarylide pigments. Pigment manufacturers estimate that only two pigments, Yellow 14 and Orange 13, are used by the rubber industry and that these were used only to the extent of approximately 63,000 lb of Yellow 14 and 12,000 of Orange 13 in 1978.

Coloration of the rubber occurs during the compounding stage. Pigments are added by two processes: dry pigment or masterbatch. The composition of a masterbatch is very similar to the color concentrate described earlier for the addition of colorants to plastics. Sources of losses and the estimated percentage loss are ~ 0.1 to 0.3% as dust during handling and mixing of the pigment, 0.1 to 0.5% in the preparation of the masterbatch, and 2.2 to 4.2% for excess rubber produced from shaping, molding, and finishing. All of these losses represent solid waste which is normally landfilled. Estimated total pigment loss from the rubber industry is summarized as follows (quantities in 1,000 lb):

	1975	1976	1977	1978
Compounding	0.05-0.1	0.07-0.2	0.08-0.2	0.08-0.2
Masterbatch	0.05-0.2	0.07-0.4	0.08-0.4	0.08-0.4
Shaping, molding, finishing	1.1-2.0	1.6-3.1	1.7-3.2	1.7-3.2
Total	1.2-2.3	1.7-3.7	1.9-3.8	1.9-3.8

Printing Ink

Printing inks, particularly the process inks used in color printing, represent the major industrial use of the pigments based on benzidine derivatives. The wide variety of printing inks range from newsprint inks to specialized electrostatic jet printing inks. However, most of the inks produced for printing can be classified into two main classes and four main types: paste inks (letterpress and lithographic) and fluid inks (flexographic and gravure).

Virtually all printing inks are produced by the batch process with some production batches exceeding 10,000 lb; more often the batches range from 100 to 500 lb. Essential steps in the production generally include:

- Weighing ingredients into mixing tub
- Dispersion of pigments into vehicle
- Adjustment of properties to product specifications
- Packaging for shipment
- Equipment cleanup (optional)

Of the pigments under study in this report, the yellows and oranges are used extensively in printing inks. The dominant pigments in terms of 1978 estimated consumption quantities were Yellow 12 (~ 11,506,000 lb), Yellow 14 (~ 1,881,000 lb), and Yellow 17 (~ 685,000 lb). Other pigments consumed by this industry include: Oranges 13 and 16 and Yellows 13, 55, and 83. Total consumption of these pigments was an estimated 15.2 million lb in 1978 or approximately 78% of the total production of all pigments under consideration in this study. Estimated consumption levels are also presented for 1975 through 1977.

The extent of production losses is markedly affected by such factors as batch size, type of ink produced (paste or liquid), the form of pigment (dry toner or flushed color), solvent or water-base vehicle, type of production equipment, and the frequency and type of cleaning system employed. For dry toner, shipping container and handling losses were estimated to be 0.05 to 0.125% whereas for flushed colors these same losses were estimated to be 0.075 to 0.1%. Losses resulting from the processing and packaging of inks depends upon the type being produced; paste inks and liquid inks are estimated to have different magnitudes of loss. Within these two main classes, differences in loss percentages will occur depending upon whether the product is solvent- or water-based. The losses associated with the various processing and packaging steps were estimated as follows:

Paste Ink	% Loss
- Oil base or solvent base, ink residue	1.5
- Oil base or solvent base, water or caustic wash	1.0
- Water base, ink residue	1.0
- Water base, water or caustic wash	3.0
Liquid Inks	
- Oil base or solvent base, ink residue	1.2
- Oil or solvent base, water or caustic wash	1.0
- Water base, ink residue	0.8
- Water base, water or caustic wash	2.5

A summary of the estimated losses of pigments resulting from printing ink manufacture for the period 1975 to 1978 is as follows (quantities in 1,000 lb):

	Solid waste	Wastewater	Total
1975	135-136	83-84	218-220
1976	183-184	113-114	296-298
1977	202-203	124-125	326-328
1978	262-264	162-163	424-427

Estimated losses of pigment for the period 1975 to 1978 arising from the subsequent use of the ink in various printing processes are summarized as follows (quantities in 1,000 lb):

	Solid Waste	Wastewater	Total
1975	950-1,536	~ 34	984-1,570
1976	1,289-2,082	~ 46	1,335-2,128
1977	1,417-2,296	~ 51	1,468-2,347
1978	1,842-2,979	~ 66	1,908-3,045

Paint and Coatings

Paints can be classed as either solvent base or water base (also called latex base), but the major production difference lies in the carrying agent. Solvent base paints are dispersed in an oil mixture, and water base are dispersed in water with added surfactant.

Practically all paints are produced using a batch process. A small paint plant may produce batches from 100 to 500 gal., while a large plant will manufacture batches up to 6,000 gal. Paint production processes consist of basically three main steps: (a) mixing and grinding of raw materials; (b) tinting and thinning; and (c) filling operations. For water base paints, the grinding step is not required.

Pigments derived from 3,3'-dichlorobenzidine and 3,3'-dimethoxybenzidine represent a small portion of all pigments used in the paint and coatings industry. While the usage of diarylide pigments is fairly widespread, it is estimated that the paint industry accounts for less than 6% of the total consumption of these pigments. The dominant pigments in terms of 1978 estimated consumption quantities were Yellow 12 (~ 356,000 lb), Yellow 17 (~ 343,000 lb), and Yellow 83 (~ 111-131,000 lb). Other pigments consumed in lesser quantities were: Yellows 13 and 14, Oranges 13 and 16, Reds 38 and 41, and Blue 25. These pigments tend to be more widely used in solvent base coatings than in water base paints and more extensively in industrial coatings than in over-the-counter sales products.

The manufacture of paint presents several principal sources at which pigments or pigment-containing paint losses can occur. The magnitude of losses throughout production and cleanup are directly affected by factors which include size and scale of operations, paint type specialization (e.g., solvent based, water based, etc.), use of dedicated equipment, equipment cleaning practices, and availability of suitable waste disposal systems. No satisfactory data were found from which industry norms for loss rates could be derived; estimated losses were derived from information provided by industry sources. Overall industry loss factors for the principal sources were estimated as follows:

Shipping container residue plus handling and weighing (100% solid waste)	0.2%
Processing and packaging waste - solvent base coatings (80% solid waste; 20% wastewater)	0.8-1.4%
Processing and packaging waste - water base paint (75% wastewater; 25% solid waste)	~ 0.6%
Equipment cleaning - solvent washing (100% solid waste)	1.0-1.5%
Equipment cleaning - water or caustic wash (30% of water reused; 70% to wastewater)	1.6%
Miscellaneous losses (50% wastewater; 50% solid waste)	0.1%

A summary of the estimated losses of pigments during paint production for the period 1975 to 1978 is as follows (quantities in 1,000 lb):

	Solid waste	Wastewater	Total
1975	7-11	2-3	9-14
1976	10-16	3-4	13-20
1977	12-18	~ 4	16-22
1978	14-21	4-5	18-26

The application of protective coatings is accompanied by significant losses due to unused paint, overspray, drop and spillage, and equipment cleanup. The fraction of paint usefully applied to the intended surface may range from less than 75% for unskilled brush painting to more than 90% for electrocoating and industrial fused powder coatings methods. Specific sources of loss were estimated; a summary of the estimated pigment losses resulting from paint application is as follows (quantities in 1,000 lb):

	Solid waste	Wastewater	Total
1975	40-71	35-55	75-126
1976	58-104	50-78	108-182
1977	67-117	56-88	123-205
1978	80-139	76-126	156-265

Textile Printing

The principal pigment consumption occurs in textile mill products where fibers have been received and transformed into some form of fabric. Except for losses of material as scrap when patterns are cut, no pigment loss occurs in the apparel industry.

There are three basic textile printing processes: roller printing, screen printing, and transfer printing. Screen printing is divided into rotary screen or flat bed screen. Typical printing processes would include the following procedures:

* Weighing ingredients into mixing tub

* Dispersion of the pigments into a paste

* Application of pigment to fabric

* Recycling excess pigment paste

* Heat curing of printed fabric

* Steaming, washing, and drying of wet printed fabric

Of the pigments under study, the following are used in varying quantities in textile printing: Oranges 16 and 34, Yellows 12, 13, 14, and 83, and Blue 25. In terms of total quantity consumed, Yellow 14 is the dominant pigment (~ 950,000 lb in 1978); other pigments with estimated consumption quantities greater than 100,000 lb in 1978 were Yellow 83 and Blue 25. Estimated consumption figures are also presented for 1975 to 1977.

Losses of pigment during textile printing operations are from the residual paste in dye containers, mixing and handling losses, excess pigment paste from printing machines, and cleanup procedures. Sources of these losses and the estimated magnitudes of each are summarized as follows:

Dust from mixing	0.05-0.10%
Residual pigment in containers	0.5-2%
Excess pigment paste - not recycled	5-20%
Cleaning waste	1-2%
Pigment in waste cloth from other finishing steps	0.7-1.0%

Based on these sources of loss, estimations of total pigment loss during textile printing operations are as follows (quantities in 1,000 lb):

	1975	1976	1977	1978
Mixing	1	1-2	1-2	1-2
Residual dye	6-23	8-34	8-34	9-35
Excess pigment loss	56-232	82-337	81-338	83-347
Cleaning waste	11-23	16-34	16-34	17-35
Waste cloth from finishing	8-12	12-17	11-17	12-17
Total	82-291	119-424	117-425	121-436

MISCELLANEOUS USES

Areas of pigment and dye consumption which were outside the scope of the major areas (i.e., home use dyes, arts and crafts dyes, marking instruments, and coloration of lubricants and fuels) and uses of the bases in laboratory and test applications are discussed.

Laboratory and Test Applications

Little information was available concerning the use of benzidine and 3,3'-dimethylbenzidine in laboratory and test applications. Information from industry indicates that the use of benzidine for occult blood tests and other laboratory procedures gradually stopped approximately 3 to 4 years ago. 3,3'-Dimethylbenzidine is used in at least one over-the-counter occult blood test kit. Consumption figures for the 3,3'-dimethylbenzidine used in these kits were unavailable.

In terms of material loss for the formulation of the pellets of 3,3'-dimethylbenzidine for the kits, it is estimated that 5% or less would be lost in formulation, probably as solid waste. The remaining 95% would be dispersed in liquid by the consumer and discarded as liquid waste to the sewer.

Home Use Dyes

These dyes are sold primarily in powder form in supermarkets, variety stores, drugstores, fabric shops, and other consumer outlets. The powdered dyes are sold in packets ranging in weight from 0.5 to 2.125 oz with commercial dye content ranging from 1% (light colors) to 45% (dark colors). Liquid dyes are sold in 8-oz containers.

Benzidine based dyes are no longer used in these formulations; however, some of these dyes may still be found on store shelves due to warehouse supplies of certain colors. The manufacturers formulate with dyes based on dimethyl- and dimethoxybenzidine (other dyes are also employed). Dyes based on 3,3'-dimethylbenzidine of interest to this study which are currently employed in home use products are Direct Blue 14, Direct Orange 6, Direct Red 2, and Direct Red 39; those based on 3,3'-dimethoxybenzidine are Direct Blue 1 and Direct Blue 218. No information was obtained from current manufacturers concerning quantities of specific dyes or general dye consumption figures for 1975 to 1978. Estimated total 3,3'-dimethylbenzidine and 3,3'-dimethoxybenzidine dye consumption levels are as follows: 1975, 230 to 255,000 lb; 1976, 190 to 215,000 lb; 1977, 140 to 195,000 lb; and 1978, 120 to 130,000 lb. These levels are for commercial dye, not active dye.

For purposes of estimating formulation losses, it was assumed that all dyes were formulated into dry packets. Using this assumption, mixing and handling losses in the formulation process were estimated to be 2 to 3%. In the home dyeing process, an exhaustion (uptake of dye on fabric) was estimated to be 25 to 40% with the remaining 60 to 75% of the dye discharged to the sewer. Estimated total losses of active dye (in 1,000 lb) are summarized as follows:

	1975	1976	1977	1978
Formulation losses	5-8	4-6	4-6	3-4
Home use wastewater	150-188	126-158	114-143	78-98
Total	155-196	130-164	118-149	81-102

Arts and Crafts Dyes

The market for arts and crafts dyes is very fragmented and little information was obtained concerning specific dyes or general types of dyes used in this area. Annual consumption of commercial dyes based on dimethyl- or dimethoxybenzidine are estimated to be very small (~ 10,000 to 20,000 lb) and has remained within that range since 1975.

It is estimated that 2,000 to 4,000 lb of commercial dye would be lost during formulation and consumer use, primarily as solid waste. The remainder is contained in or on the finished product.

Marking Instruments

Pigments derived from 3,3'-dimethylbenzidine (Orange 15) and 3,3'-dimethoxybenzidine (Orange 16) were used from 1975 to 1977 in the production of childrens crayons, lumber marking crayons, china marking pencils, paint sticks, carpenter markers, and other similar products. Orange 15 is no longer produced in the United States and the stated 1978 import quantities were very low. The estimated total consumption quantities of the two pigments are as follows: 1975 (93-98,000 lb), 1976 (107-112,000 lb), 1977 (96-101,000 lb), and 1978 (66,000 lb).

Most of these products are formulated in basically the same manner. A mixture of waxes or gums and pigment is combined to form either a liquid wax mixture, which is poured into molds, or a dough-like mass that is extruded. Estimated losses during manufacture were estimated to be 0.5% due to weighing and handling losses and 2.5 to 3.5% from trimmings or other miscellaneous losses from the cast or extruded crayons. All losses from the production process would likely be treated as solid waste. Total estimated losses from the crayon production process were estimated to be 3,000 to 4,000 lb annually from 1975 to 1977 and approximately 3,000 lb in 1978.

PRELIMINARY MATERIALS BALANCE

Preliminary materials balances were derived for BAB dyes and pigments based on 3,3'-dichlorobenzidine, 3,3'-dimethoxybenzidine, and 3,3'-dimethylbenzidine produced in the United States from 1975 to 1978.

BAB Dyes

A materials balance for the production process of BAB dyes was presented earlier in this section (see Dye Production, Table 2-2). An estimated materials balance for BAB dyes in the use areas considered in this study is shown in Table 2-4.

Pigments

Losses of 3,3'-dichlorobenzidine, 3,3'-dimethoxybenzidine, and 3,3'-dimethylbenzidine during their manufacturing process and subsequent usage to produce the pigments of interest to this study were presented earlier in the pigment production subsection. Also presented in that subsection were estimated data for pigment loss due to transfer and handling at the manufacturing site. An estimated materials balance for the pigments in the various use areas is shown in Table 2-5.

TABLE 2-4. ESTIMATED MATERIALS BALANCE FOR BAB DYES BY USE AREA

	Quantities (1,000 lb)[a]			
	Textile	Leather	Paper	Home dyes[b]
Final Product				
1975	642-2,170	357-817	611-1,081	19-65
1976	592-2,754	455-1,114	843-1,616	15-54
1977	601-2,270	522-1,088	787-1,355	14-63
1978	508-1,794	585-1,304	501-920	13-36
Losses				
Solid waste:				
1975	18-38	53-174	39-168	3-6
1976	20-48	69-236	55-250	3-5
1977	18-39	75-232	50-210	2-5
1978	15-32	86-277	32-142	2-4
Liquid waste:				
1975	112-920	0.1-0.2	0.1-0.2	69-96
1976	126-1,160	0.1-0.2	0.1-0.3	57-81
1977	112-960	0.1-0.2	0.1-0.2	42-74
1978	91-760	0.1-0.3	0.1	36-49
Air losses:				
1975	neg.[c]	0.1-0.2	0.1-0.2	neg.
1976	neg.	0.1-0.2	0.1-0.3	neg.
1977	neg.	0.1-0.2	0.1-0.2	neg.
1978	neg.	0.1-0.3	0.1	neg.

Summary

	1975	1976	1977	1978
Total dye in final products	1,629-4,133	1,905-5,538	1,924-4,776	1,607-4,054
Losses				
Solid	113-386	147-539	145-486	135-455
Liquid	181-1,016	183-1,241	154-1,034	127-809
Air	neg.	neg.	neg.	neg.
Total Losses	294-1,402	330-1,780	299-1,520	262-1,264

---

[a] Quantities are in terms of 100% dye, not standardized commercial dye.

[b] Includes arts and crafts uses.

[c] Negligible losses.

TABLE 2-5. ESTIMATED MATERIALS BALANCE FOR 3,3'-DICHLOROBENZIDINE, 3,3'-DIMETHYLBENZIDINE. AND 3,3'-DIMETHOXYBENZIDINE BASED PIGMENTS IN USE AREAS

	Quantities (1,000 lb)					
	Printing ink	Textile printing	Plastics	Coatings	Rubber	Misc. Uses[a]
Final product						
1975	6,033-6,662	827-1,076	689-843	481-498	46-47	89-95
1976	8,189-9,026	1,221-1,567	954-1,139	690-709	69-71	103-109
1977	8,997-9,063	1,196-1,574	1,023-1,251	784-811	73-75	92-98
1978	11,698-12,921	1,229-1,613	1,122-1,366	949-980	71-73	63
Losses						
Solid waste:						
1975	1,085-1,672	71-268	42-135	7-11	~1-2	3-4
1976	1,472-2,266	103-390	58-183	10-16	~2-4	3-4
1977	1,619-2,499	186-391	62-200	12-18	~2-4	3-4
1978	2,104-3,243	104-401	68-218	14-21	~2-4	~3
Liquid waste:						
1975	117-118	11-23	Neg.[b]	2-3	Neg.	Neg.
1976	159-160	16-34	Neg.	3-4	Neg.	Neg.
1977	175-176	16-34	Neg.		Neg.	Neg.
1978	228-229	17-35	Neg.	4-5	Neg.	Neg.

SUMMARY

	1975	1976	1977	1978
Total production range including imports	10,418-10,568	14,310-14,455	15,510-15,765	19,316-19,571
Total pigment in final products	8,165-9,221	11,226-12,621	12,165-13,772	15,132-17,016
Losses				
Solid	1,209-2,092	1,648-2,863	1,799-3,116	2,295-3,890
Liquid	130-144	178-198	195-214	249-269
Air	Neg.	Neg.	Neg.	Neg.
Total	1,339-2,236	1,826-3,061	1,994-3,330	2,544-4,159

[a] Crayons and other marking instruments.

[b] Negligible.

SECTION 3

DYE PRODUCTION

A number of commercial bisazobiphenyl (BAB) dyes are being produced from three bisaminobiphenyl (BAMB) precursors: benzidine, 3,3'-dimethylbenzidine, and 3,3'-dimethoxybenzidine.* Colour Index (1971) lists over 500 BAMB-based dyes that have been produced commercially. The following subsections briefly describe BAB dye production processes; the source of materials loss during dye production; production import sales, and use data for these dyes; and the estimated materials balance for dye production processes.

PRODUCTION PROCESSES

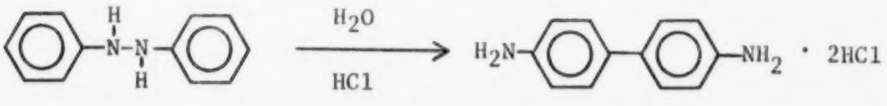
The manufacture of BAB dyes from benzidine, 3,3'-dimethylbenzidine, or 3,3'-dimethoxybenzidine involves several steps. The active dye is synthesized using a series of batch processes carried out over a range of pHs, temperatures, and reaction times. These series of operations effect the tetrazotization of the BAMB raw material, followed by the coupling of the respective tetrazo intermediate with the appropriate chemical moieties to yield the desired structure and precipitation of the crude dye product (suspension). The suspension is then filtered. The filter cake from the filtration step is further processed and diluted to yield the commercial dye. Typically, commercial dyes of this type contain from ~ 30 to 50% actual active dye.

The overall reaction for the tetrazotization and coupling steps in production of a BAB dye for example, Direct Blue 6 is shown on the following page (Kent, 1974).

The 3,3'-dimethoxybenzidine and 3,3'-dimethylbenzidine based dyes are not synthesized from precursors actually produced from benzidine. Rather, these dimethoxy and dimethyl precursors are produced from o-nitrochlorobenzene and o-nitrotoluene, respectively.

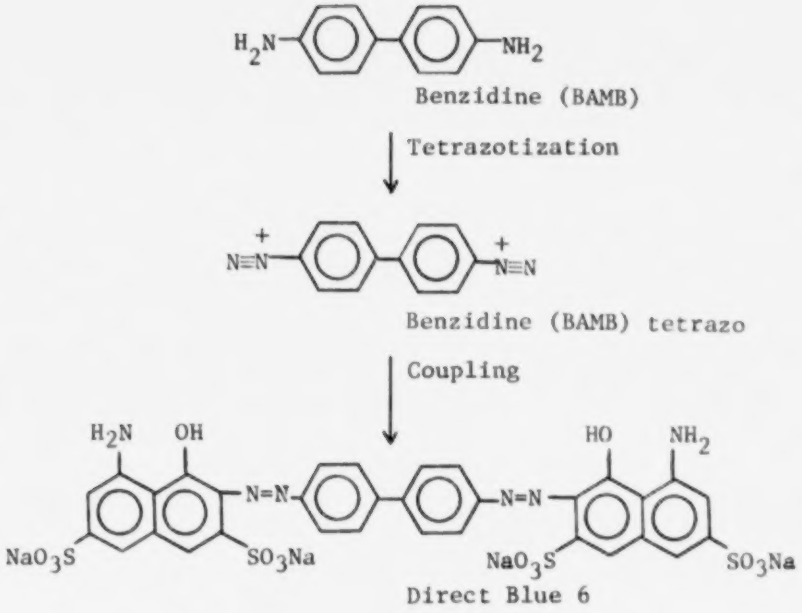
---

* Benzidine based dyes are apparently being produced from hydrazobenzene rather than directly from benzidine as shown in Equation (3-1) (Keinath, 1976). The hydrazobenzene, purchased from a supplier, is charged into a closed reactor and rearranged to benzidine hydrochloride upon the addition of water and muriatic acid:



Hydrazobenzene

Benzidine hydrochloride



(3-1)

Direct Blue 6, with a molecular weight of 936, is in the midrange of size for BAMB based dyes. These dyes generally range in molecular weight from ~ 600 to ~ 1,100, with the lower molecular weight dyes having relatively simple moieties coupled to the appropriate tetrazo compound.

The specific process used for the production of a given dye is generally quite complex. Kent (1974), for example, gives the following description of the manufacturing process for an azo dye.

> "p-Aminoacetanilide is suspended in water in a wooden or brick-lined tub (tub 2) equipped with an agitator. Two moles of hydrochloric acid per mole of amine are added, and the whole is brought to a boil by passing in live steam. As soon as the p-aminoacetanilide has dissolved, ice is added. One mole of sodium nitrite, in solution in tank 1, is run in slowly for about 2 hr. In the meantime, two moles of p-cresol are dissolved in an excess of soda ash in water (tub 3), and to this the contents of tub 2 are added with stirring. Enough ice is added to keep the temperature at about 5°C. The dye separates in part as the coupling proceeds. When coupling is complete, the contents of tub 3 are warmed with steam."

DETO (1980) provided the following description of a process for the commercial synthesis of Direct Blue 15.

Step 1 - Tetrazotization: Charge 3,000 lbs water at 15-20°C to tetrazo tank. Charge 244 lbs 100% 3,3'-dimethoxybenzidine as the dihydrochloride. Stir for 1 to 2 hr to give uniform slurry. Charge 350 lbs 20° BAUME hydrochloric acid to tetrazo tank. Stir for 1 h. Ice tank to 4 to 6°C. Diazotize with 138 lb real sodium nitrite by addition of a solution over 15 to 30 min maintaining 5 to 10°C with ice as needed. Stir for 1 h at 5 to 10°C maintaining positive test for excess nitrite throughout. Destroy any excess nitrite with sulfamic acid.

If tetrazo is not clear solution, it can be clarified into coupler using activated carbon and diatomaceous earth.

Step 2 - Preparation of Coupler Solution: Charge 6,500 lb of water at 15 to 20°C to coupler tank. Charge 730 lb H acid (4-amino-5-hydroxy-2, 7-naphthalene disulfonic acid) to tank. Bring into solution by adjusting pH to 7 to 8 with sodium hydroxide solution. Charge 550 lb sodium carbonate to coupler tank, and ice tank to 10 to 12°C.

Step 3 Coupling: Clarify or pump tetrazo solution to coupler tank maintaining 6 to 12°C. Stir at 6 to 12°C to complete coupling. Heat tank to 75 to 80°C. Charge 15% salt on volume to complete precipitation of crude dye (suspension).

The crude dye suspension is then filtered at 75 to 80°C to yield dye presscake which is washed with 15% salt solution at 70 to 75°C until the filtrate becomes pale colored.

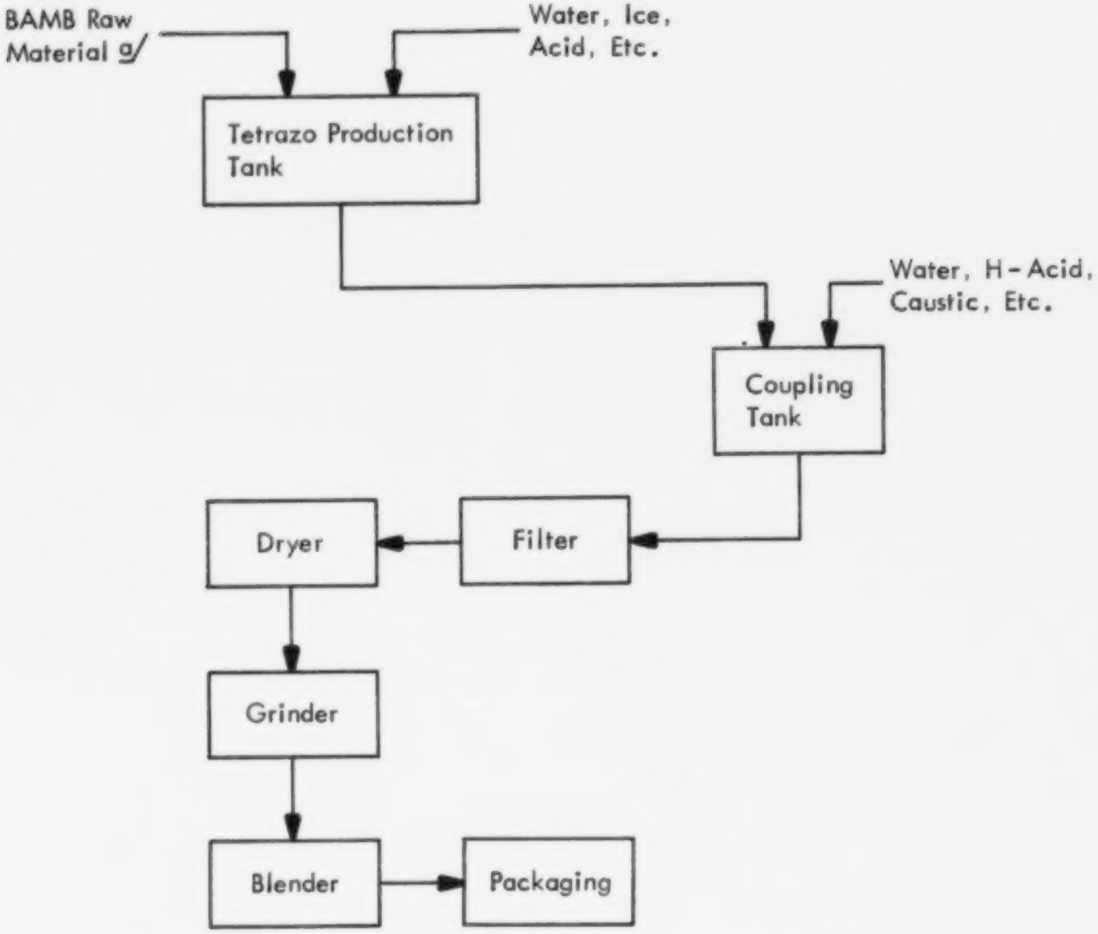
The presscake is then dryed at 95-100°C. The dried presscake is then ground and blended to form a standardized dye, as shown in Figure 3-1.

The yield of saleable dye in commercial production can range from ~ 76 to ~ 93% based on the starting BAMB raw material, depending on the particular dye and production process involved.

Even small operating problems or the lack of operator attention to detail can result in a 10% reduction of yield. Quality and yield problems can also be caused by high levels of impurities in the raw materials.

SOURCES OF LOSSES DURING DYE PRODUCTION

Losses of BAMB based materials from dye production processes have not been well quantified. This is due in part to the wide range of losses experienced because of differences in the various dye production processes, specific plant characteristics, and process control (e.g., operator error). Keinath (1976) provided valuable information regarding the presence of benzidine in dye production wastewaters. These data have been supplemented by information obtained from industry sources, project consultants, and MRI estimates in order to develop a materials balance for BAMB raw materials in the dye production processes.


BAMB Raw Material a/
Water, Ice, Acid, Etc.
Tetrazo Production Tank
Water, H-Acid, Caustic, Etc.
Coupling Tank
Filter
Dryer
Grinder
Blender
Packaging

a/ Benzidine, 3,3'-Dimethylbenzidine, or 3,3'-Dimethoxybenzidine

Figure 3-1. Example of BAB dye manufacturing process.

The following section presents a summary of the dye production losses identified during this study. Loss data are expressed in terms of the percent of the original BAMB raw material, i.e., benzidine,* 3,3'-dimethylbenzidine, and 3,3'-dimethoxybenzidine, lost during the production processes.

These loss estimates, however, should not be interpreted as estimates of emissions to the environment. Rather, they indicate estimates of starting raw material loss with respect to product yield.

Process Vent System

Current dye production processes are generally closed systems with all transfers between reactor vessels made through enclosed piping systems (Keinath, 1976). There is a potential, however, for material to be drawn into the production equipment vent system. The maximum amount of BAMB-based material going to the process vent system is estimated to be 0.1%, either in the form of unreacted starting material or as decomposition products.

By-Product

The largest loss of BAMB raw material results from the production of unwanted by-products or degradation products during the production processes. Some of these by-products remain in the finished product, while most are removed during the production and product filtration process. The range of raw materials loss to by-product is typically 5 to 15%. As previously pointed out, lack of close control of process conditions can significantly increase the rate of by-product generation.

Process Losses

Losses of material during the synthesis process result from pumping losses, spills, leaks, and intermediate purification (Fabricolor, Inc., for example, reportedly filters the hydrazobenzene before it is used to form the final product (Keinath, 1976)). These process losses are estimated to account for practically zero (~ 0.25%) to 1% of the BAMB raw material. The composition of the BAMB-based material lost during processing is assumed to be 5 to 15% by-products, 85 to 95% dye.

Production Filtration

The crude dye product (suspension) is generally filtered with a plate and frame or other type of filter press. The filtrate from this operation removes most of the by-product impurities, but also contains some of the product dye as well as some unreacted BAMB raw material. It is estimated that 1 to 3% of the starting BAMB raw material (now in the form of the BAB dye product), is lost in the filtrate. The concentration of unreacted BAMB raw material in the filtrate is estimated to be $\leq$ 0.5 ppm.

Drying, Grinding, Standardization, and Packaging

The wet filter cake from the product filtration step is normally washed and then blown with compressed air to remove adhering mother liquor (Kent, 1974).

---

* See footnote on page 3-1.

The filter cake is then dried using spray driers, circulating air, vacuum, or drum driers. The dried filter cake (presscake) is ground and diluted (standardized) to yield a product of predetermined, standard strength (dyeing intensity). Typically, these standard strength dyes contain ~ 30 to 50% actual active dye. The finished product is then packaged for sale. An estimated additional 1 to 5% of the active dye is lost during the drying-grinding-standardization-packaging process. The undiluted crude dye (i.e., the dried presscake before standardization) is estimated to contain ≤ 20 ppm unreacted BAMB raw material and 10 to 15% salt.

Raw Material Carryover

Traces of unreacted BAMB raw material can be found in the finished dye product. Commercial benzidine based dyes are usually certified to contain ≤ 10 ppm of benzidine.

Boeniger (1979) reported results of the analysis of 26 randomly collected domestic benzidine-based dye samples. Seventy-three percent of these samples contained ≤ 10 ppm of benzidine and its salts (range = 4 to 270 ppm).

For purposes of the analysis, it has been assumed that the average content of the respective BAMB raw material is ≤ 10 ppm for all BAB dyes.

Process Wastewater

Most of the unreacted BAMB material from the dye production processes eventually ends up in the process wastewater. Sources of wastewater from dye production include (a) cleaning water from slurry and salt tanks, (b) mother liquor from product filtration, and (c) water from air pollution control devices, worker showers, and floor washdown. Sufficient data on the BAMB raw material content of these wastewaters were not available to estimate environmental emissions. However, effluent standards have been established for the content of benzidine in the effluent from benzidine manufacturers* (EPA, 1977). These effluent standards call for the discharge of ≤ 0.130 lb of unreacted benzidine for each 1,000 lb of benzidine produced; this equals a benzidine loss of ≤ 0.013% of the original quantity of benzidine used.

For purposes of this analysis, it is assumed that this effluent standard is being met by benzidine based dye manufacturers, and that the emission level (≤ 0.013%) is also being met by manufacturers and users of 3,3'-dimethylbenzidine and 3,3'-dimethoxybenzidine.

PRODUCTION OF BAB DYES

The most comprehensive source of information on the domestic production of BAB dyes is the synthetic organic chemicals production data for commercial forms of dyes published by the U.S. International Trade Commission (ITC). At this writing, their data are available for 1975 through 1978. There are major limitations in the use of these data; however, in developing a detailed materials balance for individual or even major categories of BAB dyes (e.g., benzidine-based, 3,3'-dimethylbenzidine-based, and 3,3'-dimethoxybenzidine-based). This difficulty results from the grouping of specific product and production data necessitated by the requirement that the ITC maintain confidentiality of individual company figures for domestic production and sales.

---

* Benzidine manufacturers are defined in this regulation to include manufacturers of benzidine based dyes.

The ITC is also the principal source of information on individual dyes being produced in the United States. In 1977 the ITC listed over 1,000 dyes as being produced by 41 domestic companies. Unfortunately, the categorization of dyes by ITC is not according to chemical structure nor origin, and thus does not facilitate development of production data for the specific BAMB precursors of interest.

The dye production profile developed during this study has been based at EPA direction on a recently completed survey of benzidine pigments and dyes (Powell et al., 1979) and modified in accordance with a more recent report from the Dyes Environmental and Toxicology Organization (DETO, 1979), an association of dye manufacturers. The survey by Powell et al., was concerned only with the major pigments and dyes and was not concerned with the numerous low volume dyes reported by DETO. The list of currently available BAB dyes addressed in this study is given in Table 3-1. Table 3-2 shows the code letters for manufacturers, importers, and distributors employed in Table 3-1.

The Powell study also reports data that document a shift in the character of the BAB dye industry in the United States in recent years. The industry has changed from 61 products manufactured by 25 companies in 1975 to 32 products produced by only nine companies in 1978. Thus a much smaller number of individual products is available from a fewer number of manufacturers.

Figure 3-2 depicts another trend that has become more pronounced in recent years. In 1975, 15 of 61 dyes (24.6%) were manufactured domestically by only one company. In 1978, however, 21 of 32 (65.6%) of the available dyes were manufactured by only one domestic firm. These factors compound the difficulty in obtaining data on the production of specific dyes or classes of dyes because of confidentiality considerations.

The available data on U.S. production, imports, and sales of BAMB based dyes in the United States for 1975 through 1978 are given in Table 3-3. The overall trend in production of benzidine, 3,3'-dimethylbenzidine and 3,3'-dimethoxybenzidine based dye is depicted in Figure 3-3.

IMPORTS AND TOTAL BENZENOID DYE CONSUMPTION

The data presented in Table 3-3 provide reported quantities of various benzidine, 3,3'-dimethylbenzidine, and 3,3'-dimethoxybenzidine derived dyes imported into the United States during 1975 through 1978. It is the opinion of numerous industry sources, including dye importers, that these quantities are understated for all years, especially for those dyes derived from benzidine.

TABLE 3-1. BAB DYES ON THE U.S. MARKET IN 1979[a]

Dye	Manufacturer, importer, or distributor
Benzidine	
Direct Black 4	JC, FAB, CKC
Direct Black 38	JC, FRAN, FAB, CKC, BUC, L&R, ORC, SSS
Direct Blue 2	JC, FAB, FRAN, L&R, ORC
Direct Blue 6	JC, FAB, CKC, L&R, SSS
Direct Brown 1A	JC, L&R
Direct Brown 2	JC, CKC, FAB, L&R
Direct Brown 6	FAB
Direct Brown 31	FAB, CKC, L&R, JC
Direct Brown 59	JC
Direct Brown 74	FAB, L&R
Direct Brown 95	CKC, FRAN, FAB, L&R, SSS
Direct Brown 154	FAB, CKC, L&R
Direct Green 1	JC, CKC, FAB, L&R, ORC
Direct Green 6	JC, CKC, FAB, L&R, ORC
Direct Green 8	JC
Direct Orange 1	ORC
Direct Orange 8	FAB, CKC, L&R, SSS
Direct Red 1	JC, CKC, FAB, L&R, ORC
Direct Red 28	CKC, FAB, L&R, ORC, SSS
Direct Red 37	JC, FAB, L&R, ORC
Direct Violet 1	JC, L&R
Direct Violet 22	L&R
Acid Red 85	CKC, FRAN, FAB
Dimethoxybenzidine	
Direct Black 91	S, CGY, CKC
Direct Black 114	CGY
Direct Black 118	S
Direct Blue 1	AC, ATL, ACY, FRAN, CGY, CKC, BUC, FAB, HSH, L&R, BAS, S
Direct Blue 8	ATL
Direct Blue 15	AC, JC, ATL, CKC, V, DUP, S
Direct Blue 22	ATL
Direct Blue 76	AC, ATL, FRAN, BAS, FAB, CKC
Direct Blue 77	S
Direct Blue 80	ATL, L&R, BAS, CKC, CGY, S, FAB, V

(continued)

TABLE 3-1 (continued)

Dye	Manufacturer, importer, or distributor
Dimethoxybenzidine (continued)	
Direct Blue 80 (s)	CKC, CGY
Direct Blue 90	S
Direct Blue 98	ATL, FRAN, HSH, BAS, CKC, S, FAB, V
Direct Blue 100	FAB, CKC
Direct Blue 151	ATL, L&R
Direct Blue 156	CGY, CKC
Direct Blue 160	FRAN, S, CGY, CKC
Direct Blue 191 (s)	FAB, CKC
Direct Blue 218	AC, ATL, S, L&R, BAS, FAB, CGY, DUP, S, V, CKC
Direct Blue 218/224 (s)	CKC
Direct Blue 224	ATL
Direct Brown 200	S
Direct Yellow 68	CGY, CKC
Direct Violet 93	CGY
Azoic Blue Composition 2	ATL
Azoic Blue Composition 3	ATL
Azoic Black Composition 4	ATL
Azoic Diazo Component 48	ATL, ALL, BUC, PCW, V
Azoic Coupling Component 3	ATL, BUC, PCW
Others	
Atlantic Printing Black 2B Pdr.	ATL
Atlantic Printing Black FOR Pdr.	ATL
Neutrazoic Black 2B Pdr.	ATL
Neutrazoic Black FOR Pdr.	ATL
Neutrazoic Black GF 167% Pdr.	ATL
Neutrazoic Black JN Pdr.	ATL
Padazoic Black GLL Pdr.	ATL
Padazoic Black RLL Pdr.	ATL
Padazoic Black 2G 150% Pdr.	ATL
Atlantic Resin Fast Blue ARL	ATL
Atlantic Resin Fast Blue BFL	ATL
Atlantic Resin Fast Blue BLA 150%	ATL
Atlantic Resin Fast Blue BLC	ATL

(continued)

TABLE 3-1. (continued)

Dye	Manufacturer, importer, or distributor
Atlantic Resin Fast Blue BRN	ATL
Atlantic Resin Fast Blue 8BGL 200%	ATL
Atlantic Resin Fast Blue 3GLL	ATL
Atlantic Resin Fast Blue 5GLL	ATL
Atlantic Resin Fast Blue 8GLN	ATL
Atlantic Resin Fast Blue LBGL	ATL
Atlantic Resin Fast Blue 6GKS	ATL
Atlantic Resin Fast Blue 8GUM	ATL
Atlantic Resin Fast Blue 9GLR	ATL
Atlantic Resin Fast Blue UGLL	ATL
Atlantic Resin Fast Blue FFBL	ATL
Padazoic Blue GP Pdr.	ATL
Padazoic Denim Indigo Blue G Pdr.	ATL
Padazoic Navy Blue WS EX Pdr.	ATL
Pontamine Blue WE Liq.	DUP
Padazoic Brilliant Indigo 3B Pdr.	ATL
Padazoic Denim Indigo Pdr.	ATL
Atlantic Printing Brown GGN Pdr.	ATL
Atlantic Printing Brown BR Pdr.	ATL
Neutrazoic Brown BR Pdr.	ATL
Padazoic Farmer Brown Pdr.	ATL
Atlantic Resin Fast Grey LVL	ATL
Superlitefast Grey LVL	CKC
Superlitefast Rubine WLKS	CKC
Dimethylbenzidine	
Acid Red 114	AC, ATL, CGY, CKC, V, FAB, S, ORC
Acid Red 167	S, ATL, CGY
Acid Black 209	CGY
Azoic Coupling Component 5	BUC, ATL, PCW
Azoic Yellow Composition 1	ATL, ALL
Azoic Yellow Composition 2	ATL, ALL
Azoic Yellow Composition 3	ATL
Azoic Orange Composition 3	ATL
Direct Blue 14	S, CKC, CGY
Direct Blue 25	FRAN, CGY, CKC, ATL, S
Direct Blue 26	ATL
Direct Orange 6	JC, ATL

TABLE 3-1 (continued)

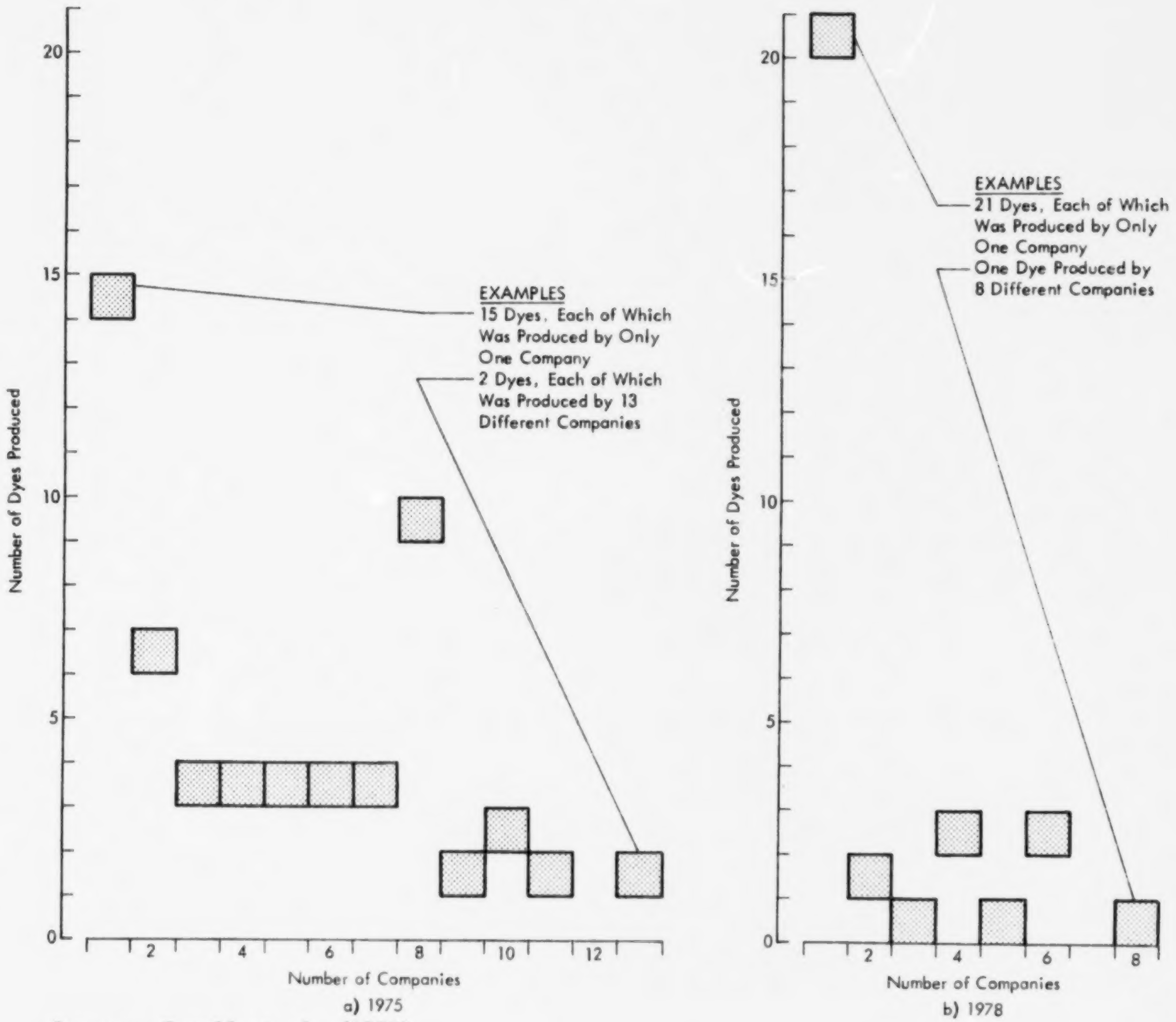
Dye	Manufacturer, importer, or distributor
Dimethylbenzidine (continued)	
Direct Red 2	AC, ATL, CKC, CGY, FAB, L&R
Direct Red 39	JC, ATL, S, CKC, L&R, ORC
Direct Brown 230	ATL
Direct Yellow 95	CGY
Others	
Diphenyl Green BBN	CGY
Pyrazol Dark Green 3B	S
Direct Fast Brown BCW-NB	ATL
Direct Fast Brown BP-NB Conc.	ATL
Direct Brown GG-NB	ATL
Direct Brown US-NB	ATL
Padazoic Yellow G Pdr.	ATL
Padazoic Golden Yellow RLL Pdr.	ATL
Padazoic Orange GR Pdr.	ATL
Penetrating Black AM-NB	CKC
Sandolan Red N-3B	S

---

a/ List derived from compilation by Dyes Environmental and Toxicology Organization (DETO), July 1979.

TABLE 3-2. CODE LETTERS OF MANUFACTURERS, IMPORTERS, AND DISTRIBUTORS

AA	American Aniline Products, Inc.
AC	American Color and Chemical Corporation
ACY	American Cyanamid Company
ALL	Alliance Chemical, Inc.
ATL	Atlantic Chemical Corporation
BAS	B.A.S.F. Wyandotte Corporation
BDO	Benzenoid Organics, Inc.
BER	Berncolors-Poughkeepsie, Inc.
BUC	Blackman-Uhler, Chemical Division of Synalloy Corporation
BUF	Buffalo Color Corporation
CGY	Ciba-Geigy Corporation
CKC	Crompton and Knowles Corporation
DUP	E. I. DuPont de Nemours and Company, Inc.
FAB	Fabricolor, Inc.
Fran	Francolor-Subsidiary of Ugine Kuhlmann Company (importer/distributor)
GAF	GAF Corporation
HSH	Harshaw Chemical Company
ICI	ICI United States
INM	Inmont Corporation
JC	John Campbell and Company (importer/distributor)
L&R	L&R International Dyestuffs Corporation (importer/distributor) (formerly L&R Dyestuffs Corporation)
NYA	Nyanza, Inc.
ORC	Organic Chemical Corporation (importer/distributor)
PCW	Pfister Chemical Ind.
PDC	Berncolors-Poughkeepsie, Inc.
PEE	Peerless Color Company, Inc.
S	Sandoz Colors and Chemicals
SSS	Sidney Springer Company (importer/distributor)
STE	Sterling Drug, Inc.
TEN	Tenneco Colors Division, Tenneco Chemical, Inc.
TOM	Toms River Chemical Corporation
V	Verona Dyestuff Division, Mobay Chemical Corporation
YOU	Young Aniline Works, Inc.



a) 1975

b) 1978

Source: Powell et al. (1979)

Figure 3-2. Characteristics of BAB dye production industry.

TABLE 3-3. U.S. PRODUCTION, IMPORT, AND SALES DATA FOR COMMERCIAL BAB DYES (in lb), 1975 to 1978

	Category[a/]	1975	1976	1977	1978
Benzidine-based dyes:					
Acid Red 85	P	67,000	72,000	72,000	39,639
	I	500	2,190	-	-
	S	66,138	75,000	-	-
Direct Black 4	P	[65,000]	[55,000]	45,000	26,444
	I	-	-	-	-
	S	[65,000]	[55,000]	-	-
Direct Black 38	P	2,168,000	3,759,000	2,245,000	823,065
	I	-	70,753	49,525	170,442
	S	2,167,122	3,923,000	-	-
Direct Blue 2	P	[250,000]	771,000	522,000	218,435
	I	11,023	38,478	-	30,755
	S	242,506	771,000	-	-
Direct Blue 6	P	[180,000]	[140,000]	287,000	61,524
	I	-	-	-	4,409
	S	[180,000]	[140,000]	-	-
Direct Brown 1A	P	-	-	-	-
	I	-	-	-	4,409
	S	-	-	-	-
Direct Brown 2	P	125,000	188,000	47,000	27,725
	I	2,205	18,739	2,205	-
	S	125,662	198,000	-	-
Direct Brown 6	P	[15,000]	[13,000]	10,500	8,563
	I	-	5,512	-	-
	S	[15,000]	[16,000]	-	-
Direct Brown 31	P	73,000	47,000	82,000	37,406
	I	-	-	-	-
	S	73,000	42,000	-	-

(continued)

TABLE 3-3 (continued)

	Category[a]	1975	1976	1977	1978
Benzidine-based dyes (continued):					
Direct Brown 59	P	-	-	-	-
	I	-	-	-	-
	S	-	-	-	-
Direct Brown 74	P	[50,000]	[45,000]	36,000	32,414
	I	-	-	-	-
	S	[50,000]	[45,000]	-	-
Direct Brown 95	P	346,000	595,000	495,000	75,953
	I	11,023	8,205	15,962	5,512
	S	406,000	532,000	-	-
Direct Brown 154	P	[230,000]	[180,000]	231,000	63,816
	I	-	-	-	-
	S	[230,000]	[180,000]	-	-
Direct Green 1	P	132,000	169,000	12,000	12,666
	I	747	-	-	-
	S	110,000	216,000	-	-
Direct Green 6	P	[135,000]	[135,000]	90,000	109,076
	I	250	-	-	4,659
	S	[135,000]	[135,000]	-	-
Direct Green 8	P	N/A	N/A	N/A	N/A
	I	-	-	250	-
	S	N/A	N/A	N/A	N/A
Direct Orange 1	P	N/A	N/A	N/A	N/A
	I	-	-	-	-
	S	N/A	N/A	N/A	N/A
Direct Orange 8	P	[70,000]	[55,000]	12,000	27,208
	I	-	4,066	-	-
	S	35,000	[55,000]	-	-
Direct Red 1	P	132,000	62,000	36,500	26,370
	I	-	-	4,409	-
	S	114,000	[60,000]	-	-

(continued)

TABLE 3-3 (continued)

	Category[a/]	1975	1976	1977	1978
Benzidine-based dyes (continued):					
Direct Red 28	P	[200,000]	[150,000]	61,000	37,327
	I	-	-	-	33,069
	S	[200,000]	[150,000]	-	-
Direct Red 37	P	63,000	N/A	N/A	N/A
	I	-	-	-	-
	S	65,000	N/A	N/A	N/A
Direct Violet 1	P	N/A	N/A	N/A	N/A
	I	-	-	-	-
	S	N/A	N/A	N/A	N/A
Direct Violet 22	P	N/A	N/A	N/A	N/A
	I	-	-	-	-
	S	N/A	N/A	N/A	N/A
TOTAL	P	4,301,000	6,436,000	4,284,000	1,627,631
	I	25,748	147,943	72,351	253,255
	S	4,279,428	6,593,000	N/A	N/A
3,3'-Dimethylbenzidine-based dyes:					
Acid Red 114	P	258,000	314,000	240,000	308,000
	I	-	3,079	24,200	-
	S	288,000	275,000	163,000	189,000
Acid Red 167	P	N/A	N/A	N/A	N/A
	I	-	-	-	-
	S	N/A	N/A	N/A	N/A
Acid Black 209	P	-	-	-	-
	I	-	-	-	-
	S	-	-	-	-
Direct Blue 14	P	[25,000]	[20,000]	[15,000]	[5,000]
	I	-	-	-	-
	S	[25,000]	[20,000]	[15,000]	[5,000]

(continued)

TABLE 3-3 (continued)

	Category[a/]	1975	1976	1977	1978
3,3'-Dimethylbenzidine-based dyes (continued):					
Direct Blue 25	P	[25,000]	[20,000]	[15,000]	[10,000]
	I	-	-	-	-
	S	[25,000]	[20,000]	[15,000]	[10,000]
Direct Blue 26	P	[50,000]	[50,000]	[50,000]	[10,000]
	I	-	500	-	220
	S	[50,000]	[50,000]	[50,000]	[10,000]
Direct Brown 230	P	-	-	-	N/A
	I	-	-	-	-
	S	-	-	-	N/A
Direct Orange 6	P	[10,000]	[10,000]	[10,000]	[15,000]
	I	-	-	-	-
	S	[10,000]	[10,000]	[10,000]	[15,000]
Direct Orange 10	P	[15,000]	[10,000]	[5,000]	-
	I	-	-	-	-
	S	[15,000]	[10,000]	[5,000]	-
Direct Red 2	P	53,000	75,000	81,000	[135,000]
	I	-	-	1,102	-
	S	46,300	57,000	64,000	128,000
Direct Red 39	P	43,000	[40,000]	[35,000]	[32,000]
	I	-	-	-	-
	S	32,000	50,000	[35,000]	[32,000]
Direct Yellow 95	P	N/A	N/A	N/A	N/A
	I	1,234	7,957	3,527	5,290
	S	N/A	N/A	N/A	N/A
Azoic Coupling Component 5	P	-	-	-	-
	I	14,409	29,903	-	6,945
	S	-	-	-	-
Azoic Orange Composition 3	P	N/A	N/A	N/A	N/A
	I	-	-	-	-
	S	N/A	N/A	N/A	N/A

(continued)

TABLE 3-3 (continued)

	Category[a]	1975	1976	1977	1978
3,3'-Dimethylbenzidine-based dyes (continued):					
Azoic Yellow Composition 1	P	N/A	-	N/A	N/A
	I	-	-	-	-
	S	N/A	-	N/A	N/A
Azoic Yellow Composition 2	P	N/A	N/A	N/A	-
	I	-	-	-	-
	S	N/A	N/A	N/A	-
Azoic Yellow Composition 3	P	N/A	N/A	-	-
	I	-	-	-	-
	S	N/A	N/A	-	-
Other[c]	P	N/A	N/A	N/A	N/A
	I	N/A	N/A	N/A	N/A
	S	N/A	N/A	N/A	N/A
TOTAL	P	479,000	539,000	451,000	515,000
	I	15,643	41,439	28,829	12,455
	S	491,300	492,000	357,000	389,000
3,3'-Dimethoxybenzidine-based dyes:					
Direct Black 91	P	[15,000]	[15,000]	[15,000]	[15,000]
	I	-	3,527	3,527	-
	S	[15,000]	[15,000]	[15,000]	[15,000]
Direct Black 114	P	-	-	-	-
	I	3,306	17,205	14,770	34,613
	S	-	-	-	-
Direct Black 118	P	-	-	-	-
	I	1,971	5,732	3,960	-
	S	-	-	-	-
Direct Blue 1	P	156,000	236,000	186,000	90,000
	I	-	-	-	-
	S	174,000	230,000	145,000	98,000

(continued)

TABLE 3-3 (continued)

	Category[a/]	1975	1976	1977	1978
3,3'-Dimethoxybenzidine-based dyes (continued):					
Direct Blue 8	P	30,000	[30,000]	[27,000]	[25,000]
	I	-	-	-	-
	S	20,000	[30,000]	[27,000]	[25,000]
Direct Blue 15	P	[325,000]	[530,000]	530,000	350,000
	I	1,896	5,726	5,393	-
	S	[325,000]	[530,000]	514,000	327,000
Direct Blue 22	P	[20,000]	-	-	-
	I	-	-	-	-
	S	[5,000]	[5,000]	[5,000]	[5,000]
Direct Blue 76	P	[75,000]	58,000	[60,000]	65,000
	I	44,000	250	250	-
	S	53,000	41,000	[60,000]	62,000
Direct Blue 77	P	-	-	-	-
	I	3,085	5,952	2,640	-
	S	-	-	-	-
Direct Blue 80	P	306,000	491,000	472,000	293,000
	I	-	-	-	250
	S	326,000	471,000	441,000	280,000
Direct Blue 80(s)	P	N/A	N/A	N/A	N/A
	I	-	-	-	250
	S	N/A	N/A	N/A	N/A
Direct Blue 90	P	-	-	-	-
	I	8,818	12,623	3,960	661
	S	-	-	-	-
Direct Blue 98	P	107,000	139,000	278,000	271,000
	I	-	-	-	-
	S	141,000	164,000	203,000	195,000
Direct Blue 100	P	N/A	N/A	N/A	N/A
	I	-	-	-	-
	S	N/A	N/A	N/A	N/A

(continued)

TABLE 3-3 (continued)

	Category[a]	1975	1976	1977	1978
3,3'-Dimethoxybenzidine-based dyes (continued):					
Direct Blue 151	P	[10,000]	[10,000]	[10,000]	[10,000]
	I	-	-	-	-
	S	[10,000]	[10,000]	[10,000]	[10,000]
Direct Blue 156	P	-	-	-	-
	I	3,857	17,415	4,630	-
	S	-	-	-	-
Direct Blue 160	P	N/A	N/A	N/A	N/A
	I	7,500	3,740	-	19,836
	S	N/A	N/A	N/A	N/A
Direct Blue 191(s)	P	N/A	N/A	N/A	N/A
	I	-	-	-	-
	S	N/A	N/A	N/A	N/A
Direct Blue 218	P	1,045,000	1,359,000	[1,000,000]	981,000
	I	-	-	-	-
	S	1,309,000	1,253,000	888,000	856,000
Direct Blue 218/ 224(s)	P	-	-	-	-
	I	-	-	-	-
	S	-	-	-	-
Direct Blue 224	P	-	-	-	-
	I	-	-	-	-
	S	-	-	-	-
Direct Brown 200	P	-	-	-	-
	I	13,558	1,543	2,204	1,984
	S	-	-	-	-
Direct Yellow 68	P	-	-	-	-
	I	14,993	14,332	14,551	1,000
	S	-	-	-	-
Direct Violet 93	P	-	-	-	-
	I	2,583	5,819	1,983	4,918
	S	-	-	-	-

(continued)

TABLE 3-3 (continued)

	Category[a]	1975	1976	1977	1978
3,3'-Dimethoxybenzidine-based dyes (continued):					
Azoic Blue Composition 2	P	–	–	–	–
	I	–	–	–	–
	S	–	–	–	–
Azoic Blue Composition 3	P	N/A	N/A	N/A	N/A
	I	–	–	–	–
	S	N/A	N/A	N/A	N/A
Azoic Black Composition 4	P	N/A	N/A	N/A	N/A
	I	–	–	–	–
	S	N/A	N/A	N/A	N/A
Azoic Diazo Component 48	P	N/A	–	–	N/A
	I	–	–	–	–
	S	N/A	–	–	N/A
Azoic Coupling Component 3	P	N/A	N/A	N/A	N/A
	I	–	–	–	–
	S	N/A	N/A	N/A	N/A
Other [c]	P	N/A	N/A	N/A	N/A
	I	N/A	N/A	N/A	N/A
	S	N/A	N/A	N/A	N/A
Total	P	1,783,000	2,377,000	2,106,000	2,100,000
	I	45,896	9,503	9,170	63,512
	S	2,052,000	2,278,000	1,867,000	1,873,000

Source: ITC (1976a, 1976b, 1977a, 1977b, 1978a, 1978b, 1979a, 1979b), NIOSH (1980a) for 1978 benzidine-based dyes, and MRI estimates. These estimates, given in parentheses, are based on information obtained from industry sources.

[a] P = Production quantity
I = Imports
S = Domestic sales

[b] N/A = Not available

[c] See Table 3-1 for dyes comprising this category.

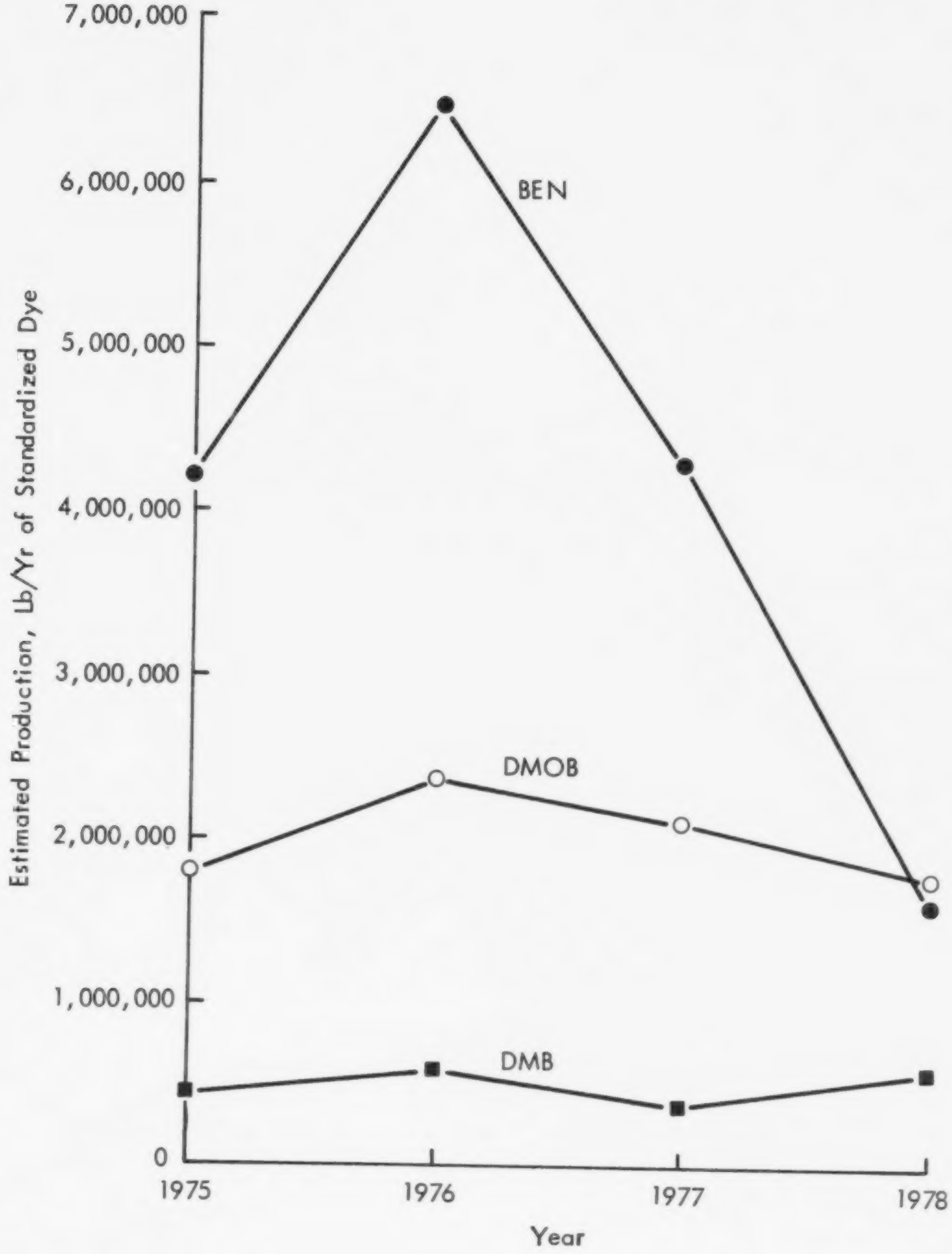


Figure 3-3. Trends in BAB dye production.

In order to provide a better insight into the actual quantities of dyes sold in the United States, and hence available for consumption, an estimated increase is required for all of the dyes of interest. Based on information provided by dye manufacturers and the Dyes Environmental and Toxicology Organization (DETO, 1980) revised data for production and imports are presented in Table 3-4 which show a considerably increased role for imports in the total quantity of dye consumed in the United States.

Estimates of the increased importation of individual dyes are not provided. It would follow that those benzidine based dyes which have been consumed in large quantities (e.g., Direct Black 38, Direct Blue 2, Direct Brown 95, and Direct Red 38) would be the most likely ones to show increased importation quantities. According to industry sources, imports of dyes based on 3,3'-dimethylbenzidine and 3,3'-dimethoxybenzidine have been at a level of approximately 20,000 to 150,000 lb annually since 1975. The very large differential between actual and reported consumption quantities has resided with the benzidine based dyes. The estimated error limits used to derive the ranges of quantities shown in Table 3-4 were generally ± 10%. This figure is in accordance with the views expressed by DETO and other industry representatives. For low volume import quantities, the MRI estimated error limits ranged from ± 10% to ± 50% with the very low import quantities assigned the higher error limits.

Benzidine based dyes imported from certain countries have been found to contain high levels (up to 224 ppm) of residual benzidine (Boeniger, 1979). Dyes from Belgium, India, Holland, Egypt, and Poland showed levels of free benzidine greater than 35 ppm. However, ITC import data do not report country of origin or quantity imported by country. Thus no means are available to estimate the total imported quantity of the highly contaminated dyes.

MATERIALS BALANCE FOR DYE PRODUCTION

Estimates have been made of the overall materials balance for the three BAMB raw materials used to make BAB dyes. These estimates have been expressed in terms of pounds of the original BAMB raw material and are summarized in Figure 3-4. The estimates presented in this figure, however, should not be interpreted as being emissions to the environment. Rather, these estimates represent losses of starting material with respect to the yield of product dye. The $\leq$ 0.5 ppm BAMB raw material in the filtrate from product filtration, for example, is typically treated in the production facility's wastewater treatment system.

Table 3-5 presents a summary of the estimated active dye losses during the production processes for 1975 through 1978. This balance is based on the sources/levels of loss previously discussed and summarized in Figure 3-4, the production rates given in Table 3-4, and the specific assumptions given in Table 3-6.

The data in Table 3-5 are expressed in pounds of active dye. For the 3.8 to 4.6 million pounds of benzidine based commercial dye production in 1975 (1.9 to 2.3 million pounds of actual active dye), for example, it is estimated that 5,000 to 26,000 lb of active dye were lost due to processing losses.

TABLE 3-4. ESTIMATED QUANTITIES OF BAB DYE CONSUMED IN THE UNITED STATES

Type of Dye	Source	Quantity (10^6 lb)[a]			
		1975	1976	1977	1978
Benzidine	U.S. production[b]	3.8-4.6	5.8-7.0	4.1-4.5[c]	1.5-1.7
	Import	0.8-1.0	0.5-0.7	1.4-1.8	2.0-2.4
	Consumption	4.6-5.6	6.0-8.0[d]	5.3-6.5	3.4-4.2[e]
3,3'-Dimethoxybenzidine	U.S. production	1.6-2.0	2.2-2.6	1.4-1.8[c]	2.5-3.1[c]
	Import	0.1-0.2	0.1-0.2	0.1-0.2	0.2-0.4[c]
	Consumption	2.0-2.4	2.1-2.5	2.5-3.1[c]	3.5-4.3[f]
3,3'-Dimethylbenzidine	U.S. production[c]	0.62-0.76	0.66-0.80	0.63-0.77	0.74-0.90
	Import[c]	0.01-0.03	0.03-0.05	0.03-0.05	0.13-0.17
	Consumption[g]	0.75-0.91	0.75-0.91	0.63-0.77	0.74-0.90

---

[a] All quantities are in terms of standardized commercial dyes; they do not represent 100% dye. To convert to active dye content, see footnote (b), Table 3-6. Estimated error limits used to derive the consumption ranges were generally ± 10%.

[b] Date from Table 3-7.

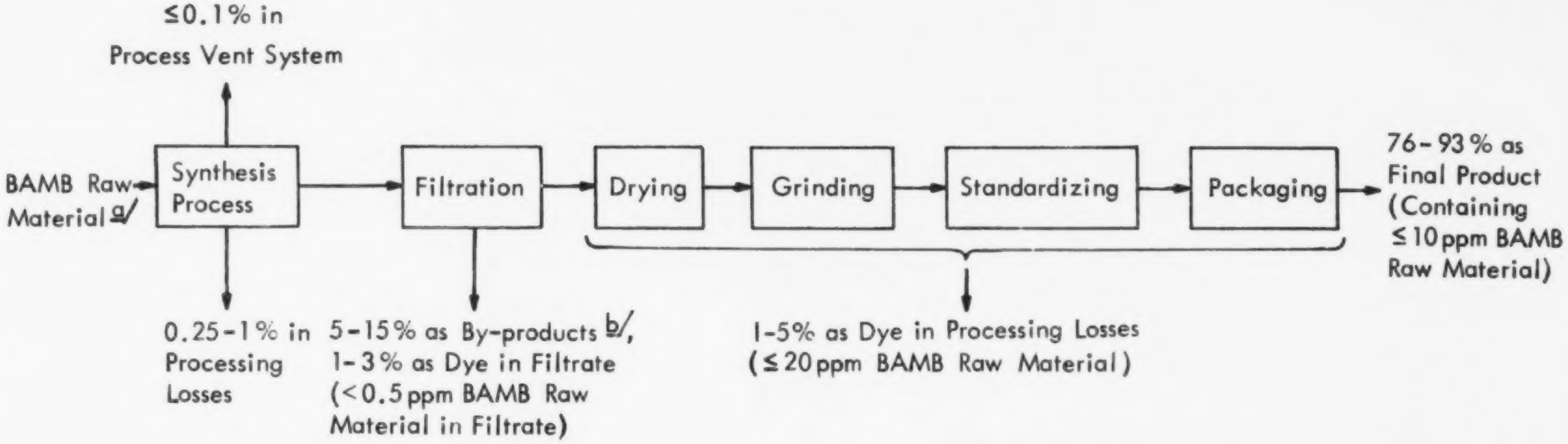
[c] Data supplied by DETO (1980).

[d] Estimated by DETO (1980) to be 5.9; estimated by MRI to be 7.0 ± 1.0.

[e] Estimated by DETO (1980) to be 3.8.

[f] Stated by the U.S. International Trade Commission (letter from J. O. Parker to S. D. Jellinek, November 19, 1979) to be 3.925 million pounds for the U.S. production quantity in 1978; estimated by DETO to be 3.9 million pounds for the 1978 U.S. consumption levele, including imports.

[g] Includes approximately 340,000 lb of dye used in numerous areas exclusive of textiles, leather, or paper. Examples of these use areas are lubricant and gasoline dyes (DETO, 1980).


≤0.1% in
Process Vent System
BAMB Raw Material a/
Synthesis Process
Filtration
Drying
Grinding
Standardizing
Packaging
76-93% as Final Product (Containing ≤10 ppm BAMB Raw Material)
0.25-1% in Processing Losses
5-15% as By-products b/, 1-3% as Dye in Filtrate (<0.5 ppm BAMB Raw Material in Filtrate)
1-5% as Dye in Processing Losses (≤20 ppm BAMB Raw Material)

a/ Benzidine, 3,3'-Dimethylbenzidine, or 3,3'-Dimethoxybenzidine

b/ Loss of BAMB Raw Material to By-products Can Be Even Higher If Close Control of Process Conditions (pH, Temperature, Mixing Times, etc.) is Not Maintained

Figure 3-4. Materials balance for BAMB raw materials in dye manufacturing.

TABLE 3-5. BAB DYE LOSSES FROM PRODUCTION PROCESSES[a]

Distribution	Active Dye Loss (1,000 lb)											
	1975			1976			1977			1978		
	BEN[b]	DMB[c]	DMOB[d]	BEN	DMB	DMOB	BEN	DMB	DMOB	BEN	DMB	DMOB
Processing losses (0.21-0.95%)[e]	5-26	< 1-4	1-8	7-40	< 1-4	2-10	5-26	< 1-4	1-7	2-10	< 1-5	2-12
Filtration losses (1-3%)	23-84	4-13	6-24	35-130	4-14	9-32	25-82	4-14	6-22	9-31	4-16	10-38
Drying, grinding, standardization, and packaging losses (1-5%)	23-140	4-22	6-40	35-210	4-23	9-53	25-140	4-23	6-36	9-52	4-26	10-63

[a] These data, which correspond to those given in Table 3-4, are on active dye basis. An overall product yield of 85% (BAMB raw material base) has been assumed.

[b] BEN = benzidine-based dyes.

[c] DMB = dimethylbenzidine-based dyes.

[d] DMOB = dimethoxybenzidine-based dyes.

[e] For the methods of calculation used in this table, see Appendix B,1.

TABLE 3-6. BASIS FOR MATERIALS BALANCE CALCULATIONS

1. Raw Materials Balance (% of raw materials)

	Range (%)
By-products	5.0 - 15.0
Process and vent losses	0.25 - 1.10
Filtration loss	1 - 3
Drying, etc., losses	1 - 5
Product yield	84[a]

2. Filtrate Rate

10 lb filtrate/lb finished (standardized) dye

3. Presscake Content of Standardized Dye[b]

Standardized Dye	Presscake Content (wt %)
Benzidine based	60
3,3'-Dimethylbenzidine based	58
3,3'-Dimethoxybenzidine based	40

4. BAMB Molecular Weights
BEN 184.2
DMB 212.2
DMOB 244.2

5. Average Dye Molecular Weight

Dye	Range (limited sample)	Calculation Value
Benzidine based	613 - 1,122	800
3,3'-Dimethylbenzidine based	620 - 1,033	750
3,3'-Dimethoxybenzidine based	775 - 969	875

---

[a] Assumed typical product yield.

[b] Weight percent presscake is standardized dye product. Dye presscake typically contains from 10 to 15% salt. Thus, actual active dye content of the presscake is 85 to 90%; a value of 85% has been used for this analysis. Using this value, the actual active dye content of the standardized dyes is calculated to be 51, 49, and 34%, respectively, for the BEN, DMB, and DMOB-based dyes.

An estimated balance has also been made for the unreacted BAMB raw material from the dye production process, e.g., the unreacted benzidine that is present in the finished product, filtrate, etc. This balance is summarized in Table 3-7. The bases for these estimates of unreacted BAMB raw material are given in footnotes on the table.

The total quantity of standardized commercial dye consumed annually during the period 1975 to 1978 was presented in Table 3-4. However, it was further developed in Table 3-6 that the percentage of active dye in the commercial product is variable depending upon whether the dye is based on benzidine, dimethoxybenzidine, or dimethylbenzidine (see Table 3-6 and accompanying footnote b). The estimated quantities of active dye (100% dye) consumed during 1975 to 1978 are shown in Table 3-8.

TABLE 3-7. UNREACTED BAMB RAW MATERIAL IN DYE MANUFACTURE[a/]

	Content (lb of unreacted BAMB raw material)											
	1975			1976			1977			1978		
Distribution	BEN	DMB	DMOB	BEN	DMB	DMOB	BEN	DMB	DMOB	BEN	DMB	DMOB
Process vent system	5-64	1-13	2-22	8-98	1-13	2-29	6-63	1-13	2-20	2-24	1-15	3-35
Processing losses	13-64	2-13	4-22	20-98	3-13	6-29	14-63	3-13	4-20	5-24	3-15	7-35
Filtration losses	2-23	< 1-4	< 1-10	3-35	< 1-4	1-13	2-22	< 1-4	< 1-9	< 1-8	< 1-4	1-16
Drying, grinding. standardization, and packing losses	46-55	7-9	13-16	70-84	8-9	18-21	49-54	7-9	11-14	18-20	8-10	20-25
Product	19-46	3-8	8-20	29-70	3-8	11-26	20-45	3-8	7-18	8-17	4-9	12-31

[a/] For the methods of calculation used in this table, see Appendix B, II.

TABLE 3-8. ESTIMATED ACTIVE DYE CONSUMPTION IN THE U.S. DURING 1975-1978

Type of dye	Quantity[a] (x 10^6 lb)			
	1975	1976	1977	1978
BEN[b]	2.3-2.9	3.1-4.1	2.7-3.3	1.7-2.1
DMOB[c]	0.7-0.8	0.7-0.9	0.9-1.1	1.2-1.5
DMB[d]	0.37-0.45	0.37-0.45	0.31-0.38	0.36-0.44

[a] Quantities in terms of 100% dye; see consumption quantities in Table 3-4 and footnote b of Table 3-6.

[b] BEN = benzidine.

[c] DMOB = 3,3'-dimethoxybenzidine.

[d] DMB = 3,3'-dimethylbenzidine.

DYE USAGE

The dye consumption data for the various use areas were derived from discussions with industry sources. The data presented for the estimated percent consumption by area in Table 3-9 are a synthesis of this information and do not represent the specific opinion of any one source. The dye industry is considerably more diffuse and much less structured than the pigments industry so that a description of the use of each dye by application is not feasible. Most industry sources agree that the percentage consumption of dyes based on 3,3'-dimethoxybenzidine and 3,3'-dimethylbenzidine has remained relatively constant from 1975 through 1978 within the three use areas. The large changes have occurred for the benzidine based dyes. For these dyes, consumption in the paper industry has declined considerably within about the last 2 years. A slight increase in usage of some dimethylbenzidine dyes has occurred but, for the most part, the substitutes for the benzidine-based dyes are not dyes based on benzidine derivatives. Consumption of benzidine based dyes in the textile industry remained relatively constant during the time period covered by this report.

TABLE 3-9. APPROXIMATE PERCENT BAB DYE CONSUMPTION BY AREA.

	1975	1976	1977	1978
Benzidine based dyes:				
Textile	50 - 60	45 - 55	45 - 55	40 - 50
Leather	20 - 25	20 - 25	25 - 30	45 - 55
Paper	20 - 25	25 - 30	20 - 25	5
3,3'-Dimethoxybenzidine based dyes:				
Textile	38 - 42	38 - 42	33 - 37	33 - 37
Leather	7 - 13	7 - 13	7 - 13	7 - 13
Paper	44 - 46	44 - 46	49 - 51	45 - 55
Other	~ 5	~ 5	~ 5	~ 5
3,3'-Dimethylbenzidine based dyes:				
Textile	44 - 50	44 - 50	36 - 41	45 - 50
Leather	6 - 9	6 - 9	5 - 8	4 - 9
Paper	3 - 6	3 - 6	5 - 8	~ 5
Other	~41	~41	~41	~41

SECTION 4

TEXTILE DYEING

This section deals with textile dyeing processes that use bisazobiphenyl (BAB) dyes. An initial industry overview is followed by a discussion of the types of textiles colored by these dyes, the quantity of the textiles colored, and the dyes used. The next subsection discusses textile dyeing processes used in the industry, and the final subsection presents an estimation of losses for the industry. A discussion of the use of pigments in textile printing is presented in Section 11.

INDUSTRY CHARACTERIZATION

Major Groups 22 and 23 of the Standard Industrial Code (SIC) cover the textile industries. Major Group 22 covers the textile mill products, and Major Group 23 covers apparel and other textile mill products.

Establishments in Group 23 primarily receive woven or knitted fabric for cutting, sewing, or packaging. Dry cleaning and auxiliary processing may be required for the manufactured products, but generally the processing is dry and involves no coloring. Except for losses of colored material as scrap when patterns are cut (10 to 20% depending on the type of pattern and fabric width), most of the losses of the dyes of interest are restricted to those in Major Group 22.

Manufacturers of textile mill products (Group 22) include 30 separate industries that manufacture approximately 90 classes of products (EPA, 1979b). Primary activities of this sector include receiving and preparing fibers; transforming these materials into yarn, thread, or webbing; converting the yarn or web into fabric or similar products; and finishing these materials at various stages of production depending on whether the product is a transitional material for another segment of Major Group 22 or intended for use by Major Group 23. Other products may be final consumer products (i.e., thread, yarn, or bolt fabric). Major Group 22 is made up of approximately 6,000 manufacturing facilities of which 70% perform operations that require no process water and 10% which require small quantities of process water. The remaining 20% generally require large quantities of process water (EPA, 1979b).

Nearly 80% of the facilities categorized as being in Group 22 are located in the Mid-Atlantic and Southern regions of the United States. The New England, North Central, and Western regions of the United States equally share the remaining 20%.

Description of Raw Materials and Fabrics Colored by Bisazobiphenyl Dyes

Fiber is the basic raw material in textile manufacturing. Coloring is not confined to fiber, however, and can be performed while goods are in the stock, top (wool or wool blends), yarn, or fabric state.

Fibers can be categorized as natural and man-made. Natural fibers include wool, cotton, flax, jute, and silk. Man-made fibers can be further divided into cellulosic and noncellulosic. Noncellulosics include polyester, spandex, aramid, fluorocarbon, nylon, polyethylene, polypropylene, acrylics, and glass. Cellulosics include rayon (regenerated cellulose), acetate (cellulose acetate), and triacetate (cellulose triacetate). In 1974 consumption of cellulosics constituted ~ 15% of domestic man-made fibers and ~ 11% of total domestic fibers; wool accounted for ~ 1% and cotton ~ 29% of total fiber consumption (Versar, 1976).

Dyes

Bisazobiphenyl dyes are classed as direct or acid dyes and may be applied to a variety of fibers. Government reports state that acid dyes are used primarily to color protein and polyamide (nylon) fibers (EPA, 1979b; Sverdrup and Parcel and Associates, 1978; Versar, 1976). Contacts with industry sources confirm this. Direct dyes are being used to color cellulosic fibers (EPA, 1979b; Sverdrup and Parcel and Associates, 1978). Versar indicates usage in cotton, rayon, polyester/cotton, and nylon/cotton (Versar, 1976). Another report indicates usage in wool, silk, and man-made fibers (Powell et al., 1979). Based on information obtained by MRI from industry contacts, it is believed that the large majority of the consumption of direct dyes involves dyeing cotton and some other cellulosics. Minor use areas might include polyester/cotton and nylon/cotton blends. Use of direct dyes to color silk could not be verified. Azoic components and compositions are insoluble pigments which are anchored within the fiber by padding with a soluble coupling compound and subsequently treating with a solution of stabilized diazonium salt. They are used for dyeing cellulosic fibers when good wet-fastness and brightness of shade at a reasonable cost is required.

The estimated production of fabric treated by BAB dyes is presented in Table 4-1. Cotton broadwoven fabric was reported as the amount dyed and finished. The Bureau of the Census reported the amounts of man-made fiber broadwoven fabric dyed in combination with the amount that was white finished (Bureau of the Census, 1978a). Eighty percent of the total amount (dyed plus white finished) was dyed (RTI, 1979). Total production of man-made fiber knit, cotton knit, and wool knit was estimated on the basis of the reported materials consumed in the production of knit fabrics. It was assumed that 80% of the total cotton and man-made fiber knits were colored and 100% of the wool knit and wool broadwoven fabric produced were colored (RTI, 1979). Only a small percentage of the knit fabrics were colored with BAB dyes.

TABLE 4-1. ESTIMATED U.S. DYED FABRIC PRODUCTION
(10^6 lb of fabric)

Type of fabric	1975	1976	1977	1978
Cotton broadwoven	512.8	541.9	510	514
Man-made fiber broadwoven	1,091.3	1,218.5	1,248	1,342
Rayon and/or acetate (including blends)	269.6	258.5	258	246
Nylon and chiefly nylon	86.3	98.8	88	92
Polyester-cotton blends	498.7	660.8	607	688
Other man-made fiber fabrics	236.7	260.4	295	316
Wool broadwoven	86.2	99.4	104	120
Cotton knit	235.6	272.6	255	244
Man-made fiber knit	1,326.4	1,183.1	1,107	1,061
Wool knit	7.8	13.8	12.3	12.3
Total	3,259.7	3,329.3	4,485	4,635

Source: MRI estimates based on Bureau of the Census Reports, 1976-1979. As part of these estimates the following conversion factors were used to convert linear yards to pounds: cotton fabric, 0.43 lb/linear yard; wool fabric, 1.025 lb/linear yard; man-made fabric, 0.44 lb/linear yard (RTI, 1979).

TEXTILE DYEING AND DYESTUFF PRINTING

Textile Dyeing

The same general dyeing process is used for the dyes of interest. Minor differences in the process are due to variations in the particular dye used, the form of the fiber (e.g., loose stock, yarn), and the type of fiber (e.g., wool, cotton, synthetic). The general process and potential sources of dye loss are shown in Figure 4-1.

The various application classes of dyes of interest are described below. Particular attention is given to the classes containing BAB dyes and to differences which pertain to dye losses.

Acid Dyes--

This class of dye has been traditionally used on wool and other animal fibers. These dyes are usually small molecules with sulfonic acid groups attached to an organic substrate. In addition to use on animal fibers, much larger quantities of acid dyes are used on nylon and other synthetic fibers for which high washfastness is needed. Exhaustion (the percentage of dye which adheres to the fabric) is usually high (95 to 98%).

Azoic Dyes--

These dyes are generally used for cellulose fibers. Dyeing with this class involves two steps: the fiber first is treated with a phenolic compound and then immersed in a solution containing a diazonium salt which couples to give a colored compound.

Developed Dyes--

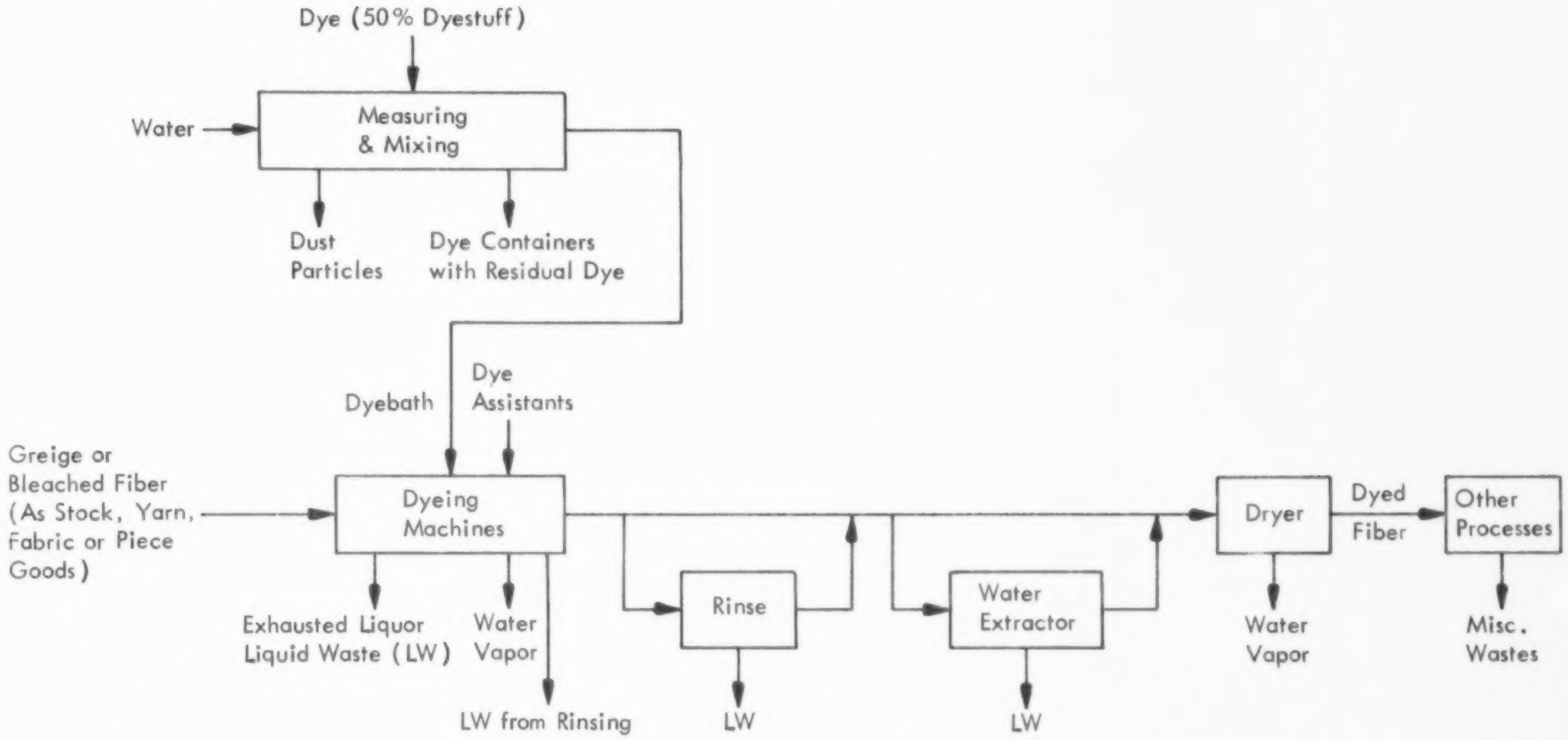
This class of dyes is similar to the azoic dyes except that the reaction steps are reversed. A dye base is used to dye the cotton and rayon fibers and then is diazotized with sodium nitrite and an acid. The diazotized dye is then reacted with other chemicals, such as β-naphthol. Direct dyes are sometimes developed to produce different shades or better washfastness and lightfastness.

Direct Dyes--

These dyes are used in neutral or basic dyebaths. Although they produce full shades on cotton and rayon, they are also used to dye wool, and synthetic fibers. Salts, such as Glauber's salt, are frequently added to increase the exhaustion of the dyebath. Exhaustion usually ranges from 70 to 95%.

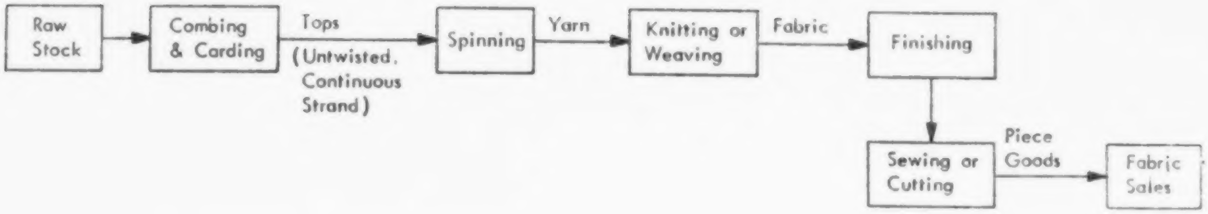
Other classes of dyes that have significant use in the textile industry include sulfur dyes, vat dyes, and fiber-reactive dyes; none of the dyes in these classes, however, are the BAB based dyes of interest to this study.

The different stages in fiber processing are shown below:


Dye (50% Dyestuff)
Water
Measuring & Mixing
Dust Particles
Dye Containers with Residual Dye
Dyebath
Dye Assistants
Greige or Bleached Fiber (As Stock, Yarn, Fabric or Piece Goods)
Dyeing Machines
Exhausted Liquor Liquid Waste (LW)
Water Vapor
LW from Rinsing
Rinse
LW
Water Extractor
LW
Dryer
Water Vapor
Dyed Fiber
Other Processes
Misc. Wastes

Source: MRI

Figure 4-1. Typical textile dyeing process.



Dyeing may occur at any stage. There are different machines used for dyeing fabric at various stages, as listed in Table 4-2. The table includes notes concerning the dye losses that occur.

Dyestuff Printing

In this process, the dyestuff is mixed with water and other components to give the paste the properties necessary for printing. Although other types of dyes, such as acid and direct dyes, are stated to be suitable for dyestuff printing, disperse dyes seem to be the major dye class presently in use. The disperse dye paste is first printed on the fabric, which then passes through a steam chamber where the dye is transferred by heat sublimation and pressure to the fabric. The fabric is then washed to remove the excess dyestuff which did not adhere.

For purposes of the materials balance, it is assumed that the vast majority of the BAB dyes used in the textile industry are used in dyeing and that very small quantities are used in textile printing. Even though very small amounts of the dyes might actually be used in textile printing, the contribution from this area to the overall materials balance is considered to be negligible for these reasons:

1. While textile printing literature mentions the use of direct dyes and acid dyes, none of the textile printers stated they were currently using appreciable quantities of either class of dye. Their use is common but the quantities used will vary according to changes in apparel styles.

2. Industry contacts indicate that the dye losses associated with dyestuff printing are comparable to losses in the dyeing industry.

ESTIMATED CONSUMPTION

This subsection contains estimated consumption data for the BAB dyes of interest to this materials balance. The complexity of the textile industry and the variability in annual consumption of specific dyes due to style change in apparel design make estimation of the consumption of specific dyes difficult. No published information is available on this subject. Industry sources were unable to provide information on the consumption of specific dyes. As a result, consumption could be estimated only by dye type (i.e., benzidine based, dimethylbenzidine based, or dimethoxybenzidine based).

TABLE 4-2. APPARATUS USED IN TEXTILE DYEING

Form of fiber	Description (and name) of dyeing apparatus	Additional notes
Loose stock	Machines generally hold stock in a compressed, dense form. Various adaptations occur to produce uniform color with circulation of dyebath.	A lower liquor ratio (10:1) may be used, resulting in better exhaustion.
Tops	Top is dyed in a ball weighing 5 to 15 lb. Machines hold balls and circulate dyebath through them.	
Yarn:		
Hank (skein)	These machines are designed with special care taken to ensure uniform coloring.	Liquor ratios tend to be higher (10:1 to 30:1).
Package	Packages may be yarn wrapped as cones, cheeses (cylinders), rockets, and tops (the form it is in immediately after spinning). The machines generally have the flow of dyebath from the inside to the outside of the package. Flow of the dyebath is typically reversed several times during a dye cycle.	
Beams	The yarn is wound on long beams and dyed on the beam.	
Fabric	Winch--A winch is used to carry the fabric into the open and back into the dyebath. Uses a continuous loop of fabric. Used mainly for woven woolens and knitted fabric. Winch is also known as beck dyeing.	
	Jig--Puts only a small amount of the fabric into the dye at one time. Usually used for cotton, rayon, and woven goods.	Very low liquor ratio.
	Padding mangle--A continuous dyeing process involving drawing the fabric through the concentrated dye solution and passing it through two rollers to give a uniform squeeze over the cloth.	
	Jet dyeing machine--A newer machine which uses a continuous loop of cloth. The cloth passes through a venturi tube. The dye liquor is circulated through the tubes and the suction at the venturi makes the fabric pass through.	Lower liquor ratio.
	Continuous dyeing machines--The fabric passes through dip troughs where the fabric is dyed, then through rinse boxes and heated drying cans.	
Piece goods	Most machines have a paddle and move the goods through the liquor. The paddle may be on one side of an oval tank; and the goods rotated around a central island. This would be the oval-type paddle. An overhead paddle machine is also available.	

Source: MRI

Direct Black 38 appears to be the most widely used BAB dye in the textile industry. This dye has a variety of uses, although the majority seems to be for coloring materials such as cambric (low grade cotton used to cover the underside of upholstered furniture). Direct Blue 218 is also widely used in the textile industry.

The estimated consumption of BAB dyes by the textile industry, developed from data in Tables 3-8 and 3-9, is presented in Table 4-3.

TABLE 4-3. ESTIMATED BISAZOBIPHENYL DYE CONSUMPTION IN THE TEXTILE INDUSTRY

Dye Type	Quantity (10^6 lb)[a] 1975	1976	1977	1978
BEN[b]-based	1.2-1.7	1.4-2.3	1.2-1.8	0.7-1.1
DMOB[c]-based	0.27-0.34	0.27-0.38	0.30-0.41	0.40-0.56
DMB[d]-based	0.16-0.23	0.16-0.23	0.11-0.16	0.16-0.22
Total	1.6-2.3	1.8-2.9	1.6-2.4	1.3-1.9

[a] See Tables 3-8 and 3-9; quantities in terms of 100% pure dye.

[b] BEN = benzidine; [c] DMOB = dimethoxybenzidine; and [d] DMB = dimethylbenzidine.

ESTIMATED LOSSES

This subsection discusses losses of dyes in textile coloration. Specific loss areas are identified, and estimated percent losses are calculated for dyes. Losses of the subject compounds are approximated.

Dye losses that occur during textile processing are in the dust from mixing operations, residual dyes in the original dye containers, and mixing and holding containers, and the liquid wastes from the dyeing, rinsing, and water extracting. Because of the low volatility of the BAB dyes, there should be very little or no loss from evaporation with the water in the dyeing and air drying stages. Sources of dye loss and estimated magnitude of the losses are shown in Table 4-4.

In one study on solid wastes from the textile industry (Versar, 1976), data were obtained on the residual dyestuff in containers for several textile industry categories. All figures for the percentage of dye loss due to residual dye in the container range from 0.02 to 0.05%. In order to apply these data to the BAB dyes, it must be assumed that the percentage of residual dye in each process category is the same for all dyes.

TABLE 4-4. ESTIMATED BISAZOBIPHENYL DYE LOSSES IN TEXTILES

Source of loss	% Lost
Dust particles	0.05-0.1
Residual dye in containers	0.02-0.05
Exhausted liquor	
Direct dyes	5-30
Acid dyes	2-5
Unrecycled dye from continuous units	2-10
Water vapor from dyeing machines (open vessels and pressure venting)	~ 0
Liquid waste from rinsing machines, rinsing cloth (fiber), and water extraction	(a)
Water vapor from dryer	~ 0
Solid wastes from processing after dyeing	1.0-1.5

Source: Versar (1976); industry sources; MRI estimates.
(a) Included in exhaust liquor.

A small percentage of dye will be lost as dust particles during weighing of the dry ingredients of the dye mixtures. Since specific data could not be found for this process, figures for the loss of dye were estimated to be the same as those for a similar mixing stage in the paint production industry.

The major loss of dyestuff in textile dyeing is the residual dye in the wastewater from dyebaths. Numerous variables enter into the exhaustion. These include the particular dye used, the fiber being dyed, the desired intensity of color, the liquor ratio, and the temperature. The large quantity of information that would be necessary to derive specific data on the loss of these dyes could not be obtained from the published literature or industry sources. Therefore, only generalizations can be made concerning the effects of change in these variables.

The desired intensity of the color makes a big difference in the exhaustion. Generally, if two batches of the same material at equal weights are dyed with the same dye but at two different intensities, the batch with the darker color will have a lower exhaustion.

The liquor ratio is the ratio of the weight of the liquor (dyebath) used to the weight of the dry fabric. The equilibrium reached in dyeing depends on the concentration of dye in the fabric and the concentration of dye in the liquor. Therefore, a higher liquor ratio tends to produce a lower exhaustion.

Although the equilibrium which pertains to the exhaustion rate is temperature dependent, this temperature dependency varies with the particular dye used. Industry sources state that because temperature also affects leveling and dyeing rates, the dyer generally does not choose the temperature of greatest exhaustion.

When used with a suitable type of fiber, direct dyes give 70 to 95% exhaustion. The exhaustion may be greater than 95% with very weak initial dye concentrations, but the total quantity of dye consumed at these low concentrations is small. Variations in this class of dyes can be attributed to the frequent use of dye assistants for some direct dyes and to other special processing such as dye development. Acid dyes usually exhibit higher exhaustion than do direct dyes. The exhaustion usually ranges from 95 to 98%, but is affected by various factors.

The estimated residual dye in the exhausted liquors were summarized in Table 4-4. This table includes estimated losses resulting from rinsing, water extraction, and dyebath cleaning.

The dyed fabric is occasionally rinsed prior to further processing operations. The rinsing step may occur in the dyeing vessel if batch dyeing is used, or it might involve a separate procedure if a continuous dyeing process is used.

Rinsing and cleaning the dye machines would result in small quantities of dye loss to wastewater. Dyers usually use lighter to darker dyebaths so less rinsing is required. More extensive cleaning becomes necessary when the machine is to be used for a light colored dyebath. This cleaning, as well as the other rinses, is done with water or a cleaning solution containing bleach.

The fate of all liquid waste is essentially the same for all of the textile dyeing facilities. All of the waste is treated by water treatment facilities, either by the company or by the municipality. American Textile Manufacturers Institute (ATMI) estimates that of the 2,007 textile plants which generate potentially hazardous waste, 488 plants have wastewater facilities. It is further estimated that the production of these 488 plants accounts for 65% of the total production of the 2,007 plants (Versar, 1976). Because no data are available for a detailed evaluation of the distribution in the use of these dyes, it is assumed that the amount of consumed dye is proportional to the production of the plants. Thus, about 65% of the dye lost in wastewater is treated by the individual companies.

Some solid waste is created by miscellaneous processing of the dyed fiber. The percentage loss by this processing is shown in Table 4-5 for the typical processes in each of the industry categories. If the percentage losses in this table are weighted by the relative production rates for each industry category, the percentage loss for all textile dyeing and finishing industries is ~ 1%. Although the average loss of BAB dyes through these processes, would be about 1.0 to 1.5%, this higher average loss percentage is because most BAB dyes are not used in dyeing wool fabrics or carpeting (the highest loss categories shown in Table 4-5). Much of the yarn and stock material will be involved in fabric processing which will produce additional loss. Generally, these wastes are disposed in a landfill.

TABLE 4-5. FIBER LOSSES DURING FINISHING AND OTHER PROCESSING STEPS

Industry category (dyeing and finishing)	Processing steps	Form of loss	Percent loss
Wool	Special and mechanical finishing	Flock and fabric	1.8
Woven fabric	Mechanical finishing	Cloth and fabric	1.0
Knit fabric	Chemical and mechanical	Cloth	0.7
Carpet	Selvage trimming and fluff shearing	Selvage and flock	3.0
Yarn and stock	Beaming, quilling, windings, etc.	Yarn	0.6

Source: Versar, 1976

Estimated total bisazobiphenyl dye losses in the textile industry are presented in Table 4-6.

TABLE 4-6. ESTIMATED BISAZOBIPHENYL DYE LOSS IN THE TEXTILE INDUSTRY

	Quantity (1,000 lb)			
	1975	1976	1977	1978
Dye consumed[a/]	1,600-2,300	1,800-2,900	1,600-2,400	1,300-1,900
Dye losses[b/]				
Dust (0.05-0.1%)	1-2	1-3	1-2	1-2
Residual dye in containers (0.02-0.05%)	1	1	1	1
Exhaust liquor (5-30%)	80-690	90-870	80-720	65-570
Unrecycled dye (2-10%)	32-230	36-290	32-240	26-190
Solid waste (1.0-1.5%)	16-35	18-44	16-36	13-29
Total	130-958	146-1,208	130-999	106-792
Dye in final product	642-2,170	592-2,754	601-2,270	508-1,794

[a/] Data from Table 4-3.

[b/] Data from Table 4-4.

SECTION 5

LEATHER TANNING INDUSTRY

INDUSTRY OVERVIEW

The leather industry is composed of companies which perform a portion of or all the steps required to produce finished leather from raw hides. Throughout the 1970's, the total number of plants has been declining. In 1972 there were over 500 establishments in the United States, but by 1977 the number had fallen to about 400 (Radding et al., 1978; EPA, 1979a). Some of the companies involved in leather tanning are quite large, but many are small, family-owned businesses. The number of employees per tannery ranges from 5 to 500, and production rates range from 100 to over 2,500 hides per day (Conrad et al., 1976; Francke et al., 1978).

The U.S. leather industry has traditionally been centered in the northeastern states. Although some tanneries have followed the supply of hides westward, there is still a concentration of tanneries in the New England and Middle Atlantic states. In 1976 about 30% of all tanneries were located in Massachusetts or New York, and about 85% were located east of the Mississippi River (Conrad et al., 1976). Fulton County, New York, provides an example of a local concentration of leather handling facilities; in 1967, 22 tanneries were located in or around the two small communities of Gloversville and Johnstown (Nemerow and Armstrong, 1967). Farther west, another concentration of tanneries is located in the Milwaukee-Chicago area. Overall tanneries are scattered across the country in 34 states (Conrad et al., 1976).

Although shoe leather is their biggest single product, a great variety of goods are marketed by U.S. tanneries. Table 5-1 presents a partial listing of the categories and types of leather available from domestic tanneries. The tremendous variety inherent in the production of these goods is accented by the changes in fashion and the multiplicity of manufacturers active in the market. Popular colors and styles in shoes, handbags, belts, and other leather goods may vary dramatically over short periods of time. When these changes do occur, companies make rapid adjustments in their processing and dye usage depending on the needs of their current clientele. Thus, different firms may be quite dissimilar in methodology and/or end products.

TABLE 5-1 A PARTIAL LISTING OF THE CATEGORIES AND TYPES OF LEATHER PRODUCED BY U.S. TANNERS

Belt and watchstrap
Bookbinding
Chamois
Craft
Glove and garment
Handbag
Harness and saddle
Hat, cap, and sweatband
Holster and tool pouch
Lace
Linings
Luggage
Orthopedic articles
Patent
Reptile and sharkskin
Shoe upper and sole
Sporting goods
Transmission belting
Upholstery

Source: Adapted from Tanners Council of America (1977).

Much of the detailed production information is highly proprietary. The reason for this concern is competition--there are approximately 100 producers of glove and garment leather and approximately 80 producers of handbag leather listed in the Tanners Council 1977 Directory (TCA, 1977).

The primary raw material for leather is cattle hide (> 90%). The other animal hides and skins that are used--sheep, lamb, and pigskin*--contribute less than 10% of the total hide tanned (Radding et al., 1978). Consequently, the leather industry is closely linked to the beef industry.

During the 1975 to 1978 period, the annual commercial cattle slaughter in the United States ranged from about 39.5 to 42.5 million head; the lowest production occurred in 1978 (U.S. Department of Agriculture, 1979). During the same period, the annual number of equivalent hides** tanned in the United States has ranged from 20 to 22 million hides, again with the lowest production in 1978 (Radding et al., 1978; Lollar, 1979). The discrepancy between total cattle slaughter and total hides tanned is due primarily to foreign acquisition of U.S. hides. Purchases by tanners in South Korea, Japan, Spain, and Italy are particularly significant (Harrison, 1979; Gallup, 1974) because after finishing, much of this leather is imported to the U.S. market for sale (Radding et al., 1978).

---

* A very small quantity of exotic hide and skin is also tanned: goat and kid, deer, elk, moose, reptile, seal, kangaroo, and shark.

** One equivalent hide = 3.7 m^2 (40 ft^2) of leather.

LEATHER TANNING AND DYEING PROCESSES

The production of leather involves four principal stages: (a) beamhouse processing, (b) tanhouse processing, (c) retanning, coloring, and fat liquoring, and (d) finishing.

Typical operations in the initial beamhouse processing include cutting the hides in half (lengthwise), washing and soaking, fleshing, and hair removal. For the washing, soaking, and chemical loosening and/or dissolution of hair--as well as many of the subsequent tanning stages--the hides are placed in processing solutions in vats (with or without paddles), drums, or hide processors (concrete mixers with special linings). Fleshing is accomplished on special machines designed for that purpose (Gallup, 1974).

At the completion of these preparatory steps, the hides are moved to the second stage in the tanning sequence, the tanhouse where they are subjected to bating, pickling, tanning, and splitting.

- Bating occurs in vats, drums, or hide processors. A solution of ammonium salts and enzymes delime the skins (the lime is a residue from the dehairing solutions), reduce swelling in the leather, peptize fibers, and remove protein degradation products.

- Pickling involves the introduction of an acid and a brine, normally into the same vessel where bating has taken place. Pickling is always carried out prior to chrome tanning, and the process is sometimes also employed prior to vegetable tanning.

- Tanning requires the treatment of the hides with chromium sulfate mixtures or vegetable (plant extract) tanning solutions. Chrome tanning in drums is the most common procedure. Vegetable tanning is used primarily in the production of heavy leathers, i.e., shoe sole leather, mechanical leathers, or saddle leathers; the process usually occurs in vats.

- Splitting involves the splitting of the tanned hide into a grain-side portion having a constant thickness and a fleshside portion, also called a "split" (Gallup, 1974).

Retanning, coloring, and fat liquoring make up the third stage in the tanning procedure.

- Retanning is a second tanning step carried out in drums to which chrome, vegetable, or synthetic tanning agents are added. This procedure yields a finished leather possessing better characteristics than those which would result if tanning was performed in only one treatment. (At this point, sole leathers are commonly bleached with sodium bicarbonate and sulfuric acid.)

- Coloring is carried out in the same drums used for retanning. Dyes may be added before or after fat liquoring. This is the stage at which the most significant dye use occurs in the leather industry. Consequently, a more thorough discussion of this portion of the tanning process is presented following the general description of the entire tanning operation.

- Fat liquoring is the replacement of oils lost from the leather during tanning. This treatment softens the leather and makes it pliable. Different quantities of oil are added to leather destined for different end uses (Gallup, 1974).

Finishing operations include drying, wet-in coating, staking or tacking (a form of massaging), and plating (a surface treatment). Some pigment and small quantities of dye may be applied to the leather surface during these operations. However, the quantities of dyes or pigments involved are insignificant compared to dye use in coloring. The finishing procedures complete the tanning operation and result in products suitable for the manufacture of leather goods (Gallup, 1974).

The most authoritative current reference on the dyeing of leather is Radding et al. (1978). Much of the information presented here is derived from this source.

Leather is dyed in a batch mode process, usually in the same drums in which the retanning and fat liquoring (addition of oils) takes place. Typically, the dye is added following retanning and prior to fat liquoring. During the coloring operation, the hides and the dye solution are mixed, commonly by the rotation of a drum (Radding et al., 1978).

The dyes used by the tanneries are most often acid or direct dyes. Basic dyes are also used, as are solvent and sulfur dyes, but acid dyes are used in the largest overall volume. Direct dyes are somewhat limited by their inability to penetrate vegetable tanned leather or blue hides (chrome tanned hides before retanning). Consequently, direct dyes are most suitable for surface dyeing applications. Both acidic and basic dyes penetrate deeper into the leather than do the direct dyes. All of the dyes used are formulated to act as protein binding compounds (Radding et al., 1978).

The predominant colors used by leather tanners are black, brown, and various other colors which are used with brown to produce shades of brown. These dyes are acquired by the tanneries in many different forms. The larger tanneries are frequently able to buy the material directly from the dye manufacturer and then formulate their own color compositions. The smaller tanneries are more apt to purchase blended dyes from companies which formulate leather tanning chemicals. Both the large and small tanneries also buy leather specialty dyes, dye formulations put out by the major dye manufacturers specifically for use in the leather industry (Lollar, 1979).

The quantity of dye required for a given application depends on many factors including color, type of leather (split or grain; cattle, sheep, etc.), and the mix of dyes. Different colors and intensities are produced using different dyes or different dye mixtures, but part of this technology also involves variations in the quantity of dye used. Typical percentages of commercial dye per wet leather weight range from 0.25 to 5.0% with an average around 0.7%, which is about 13 lb of commercial dye per 2,000 lb of wet leather (Radding et al., 1978).

The specific bisazobiphenyl (BAB) dyes used in leather tanning are difficult to pinpoint for any given year due to changes in demand for different colors on different products. The abundance of proprietary formulations, whose composition cannot be obtained, is also a major problem (Radding et al., 1978). However, some BAB dyes are known to have been used in the leather industry during the 1975 through 1978 period. These dyes are listed in Table 5-2.

DYE CONSUMPTION

Knowledge of the quantity of dyes used by a tannery can be used to estimate their total production of finished hides. Since this information is an important marketing tool, the extent and nature of dye utilization within individual tanneries is highly proprietary.

Estimates of the quantity of BAB dyes consumed in the leather industry are presented in Table 5-3. The dyes of interest to this study that are consumed in the leather industry were presented in Table 5-2.

As a check of the validity of the estimations employed in the derivation of the quantities in Table 5-3, an alternative method was employed to estimate the quantities of BAB dyes in the leather industry.

Approximately 85% of all tanned hides are dyed (Lollar, 1979). The average usage of dye amounts to approximately 0.7% of the weight of hide dyed, with an average weight per hide of 50 lb (Radding et al., 1978; Lollar, 1979). Table 5-4 shows the total number of hides tanned from 1975 through 1978 and the corresponding dye consumption based on these estimations.

In order to estimate the fraction of the leather industry's total dye consumption that was BAB dyes, MRI conducted a literature search and contacted individuals within the leather industry. Information obtained from these two sources indicated:

1. Approximately 38%* by weight of the dye sold in 1975 to U.S. tanneries was direct dye (Radding et al., 1978).

---

* Total dye sales to the leather industry during 1975 were ~ $15 million at an average price of $3.00/lb. These figures indicate total dye sales of ~ 5.0 million lb. Direct dyes accounted for $3.7 million worth of this total at an average price of $1.95/lb. Thus direct dye sales are approximately 1.90 million lb (Radding et al., 1978). Based on these statistics, direct dye purchases accounted for ~ 38% of total dye purchases by weight during 1975.

TABLE 5-2. BAB DYES USED IN LEATHER TANNING, 1975-1978[a]

Benzidine-based dyes		o-tolidine-based dyes (3,3'-dimethyl . .)		o-dianisidine-based dyes (3,3'dimethoxy . .)	
CI No.	Generic name	CI No.	Generic name	CI No.	Generic name
22245	Acid Red 85[b]	23635	Acid Red 114	30400	Direct Black 91
302455	Direct Black 4	23850	Direct Blue 14	24410	Direct Blue 1[b]
30235	Direct Black 38[b]	23790	Direct Blue 25	24400	Direct Blue 15
22590	Direct Blue 2	31930	Direct Blue 26	24280	Direct Blue 22
22610	Direct Blue 6	23375	Direct Orange 6	24411	Direct Blue 76
22311	Direct Brown 2[b]	23370	Direct Orange 10		
30140	Direct Brown 6	23500	Direct Red 2	23155	Direct Blue 98
35660	Direct Brown 31[b]	23630	Direct Red 39[b]	24175	Direct Blue 151
36300	Direct Brown 74[b]				
30145	Direct Brown 95				
30120	Direct Brown 154				
30280	Direct Green 1				
30295	Direct Green 6				
22310	Direct Red 1				

[a] Adapted from Powell et al. (1979).

[b] Usage confirmed by industry contacts.

TABLE 5-3. ESTIMATED CONSUMPTION OF BAB DYES IN THE LEATHER INDUSTRY

Dye category	Quantity (1,000 lb)[a/]			
	1975	1976	1977	1978
BEN[b/]	460-725	620-1,025	675-990	765-1,155
DMOB[c/]	49-104	49-117	63-143	84-195
DMB[d/]	22-41	22-41	16-30	14-40
Total	531-870	691-1,183	754-1,163	863-1,390

a/ Data derived from Tables 3-8 and 3-9; 100% pure BAB dye, not standardized commercial dye.

b/ BEN = benzidine-based.

c/ DMOB = 3,3'-dimethoxybenzidine-based.

d/ DMB = 3,3'-dimethylbenzidine-based.

2. Approximately 68 to 75% of the direct brown and direct black dye sold in the United States during 1975 and 1976 was BAB dye (Jenkins, 1978).

Table 5-5 combines the available information and estimates to yield an approximate total consumption of BAB dye by the leather industry. The total quantity of dye consumed is calculated using the method of Radding et al. (1978) with a minor change in accord with comments by Lollar (1979). The approximate levels shown in Table 5-5 for BAB dye consumption for 1975 to 1978 generally fall within the range estimated by a completely different method in Table 5-3.

ESTIMATED LOSSES

The discussion which follows presents an estimation of the total quantity of BAB dye which remains a part of finished leather goods and the quantity of BAB dye that becomes a constituent of production waste. The estimates required to quantify dye uptake are taken from Radding et al. (1978). This source indicates that about 85 to 90% of the dye utilized in leather dyeing is successfully joined to the leather. In order to allow for trimmings,

TABLE 5-4. OVERALL DYE CONSUMPTION IN THE LEATHER INDUSTRY (1975-1978)

	Total number of hides tanned in the U.S.[a] (10^6)	Number of dyed hides[b] (10^6)	Weight of dyed hides[c] (10^6 lb)	Weight of total dye consumed[c] (10^6 lb) (0.7% of dyed hide weight)
1975	22	19	950	6.8
1976	24	20	1,000	7.1
1977	22	19	950	6.8
1978	20	17	850	6.0

[a] Statistics obtained from Radding et al. (1978) and Lollar (1979). For purposes of this approximation, 1 hide = 40 ft^2 of leather.

[b] ~ 85% of the total; obtained from Lollar (1979).

[c] 50 lb per hide; method of approximation patterned after Radding et al. (1978).

TABLE 5-5. APPROXIMATE CONSUMPTION OF BAB DYE BY THE LEATHER INDUSTRY (1975-1978)

	Quantity of dye consumed[a] (0.7% of dyed hide weight) (10^3 lb)	Percent direct dye[b] (%)	Direct dye consumed (10^3 lb)	Percent of direct dyes which are BAB dyes[c] (%)	Standardized BAB dye consumption (10^3 lb)	Active BAB dye consumption[d] (10^3 lb)
1975	6,800	~ 35	2,400	~ 65	1,600	787
1976	7,100	~ 35	2,500	~ 65	1,620	802
1977	6,800	~ 35	2,400	~ 65	1,600	787
1978	6,000	~ 45	2,700	~ 65	1,750	858

[a] Adapted from Radding et al. (1978) and Lollar (1979); see Table 5-4.

[b] MRI estimates based partially on Radding et al. (1978).

[c] MRI estimates based partially on Jenkins (1978). Personal communications with leather industry sources were inconclusive in regard to changes in BAB dye consumption (Lollar, 1979; anonymous industry sources). However, one dye manufacturer indicated that the leather industry has been slower to reduce its usage of BAB dyes than the other major consuming industries.

[d] Active BAB dye consumption derived from the weighted quantity of pure BEN, DMOB, and DMB contained in 1,000 lb of standardized commercial dye. Percentage composition of 1,000 lb of "BAB" dye obtained from Table 5-3. Percentage of pure dye contained in standardized dye taken from footnote (b) of Table 3-6.

buffing losses, and other miscellaneous losses, the lower end of this range is reduced to 80%. Consequently the final range used for the calculation of BAB dye retention on finished leather goods is 80 to 90%.

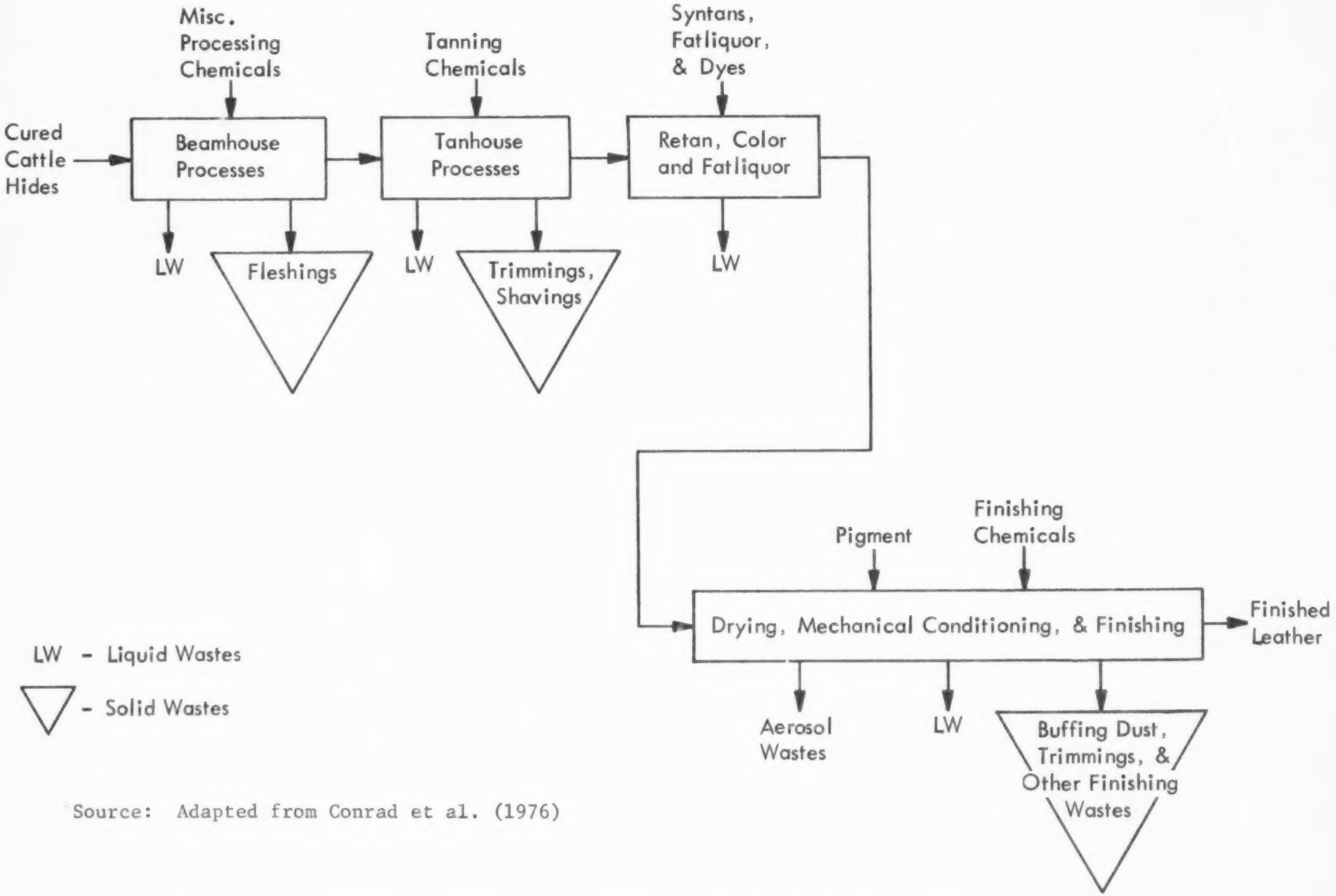
The remaining 10 to 20% of the dye consumed in processing enters production waste streams (note Figure 5-1). Although no definitive information is available to provide a quantitative breakdown for the fate of waste dyestuffs in leather tanneries, some relevant facts are known. The dyes in question are protein binding formulations (Radding et al., 1978). Proteinaceous materials abound in the liquid effluents which result from leather tanning processes (Conrad et al., 1976; MRI, 1977). Aerosol losses during the mixing of dyes and the drying of dyed leather may account for a minor loss of dye material, but no evidence is available to quantify these losses. All of this evidence indicates that the majority of the BAB dye that is lost in processing will ultimately become a solid waste--either as a component of a wastewater sludge or as a component of plant buffing dust, trimmings, or other miscellaneous solid waste residues. Additional losses to solid waste will occur during subsequent industrial fabrication of leather products.

Consequently the fate of the BAB dyes lost during the coloring of leather, which represents 10 to 20% of the total dye consumption, is thought to be greater than 99.8% solid waste, less than 0.1% liquid waste, and less than 0.1% aerosolized waste. No basis exists for an industry-wide breakdown specifying the portion of the BAB dye waste that appears in wastewater sludge, leather trimmings, buffing dust, or other miscellaneous residues. However, Conrad et al. (1976) suggest that the percentage breakdown for all tannery solid wastes is as follows:

60%	Wastewater screenings and sludge
35%	Trimmings and shavings
3%	Floor sweepings
2%	Finishing wastes

Dye could be present in small quantities in any of these four categories.

Table 5-6 summarizes the estimated losses of BAB dyes in the leather industry during the 1975 through 1978 period. The total dye consumption figures are based on MRI estimates described earlier in this section (Table 5-3).


Misc.
Processing
Chemicals
Tanning
Chemicals
Syntans,
Fatliquor,
& Dyes
Cured
Cattle
Hides
Beamhouse
Processes
Tanhouse
Processes
Retan, Color
and Fatliquor
LW
Fleshings
LW
Trimmings,
Shavings
LW
Pigment
Finishing
Chemicals
Drying, Mechanical Conditioning, & Finishing
Finished
Leather
Aerosol
Wastes
LW
Buffing Dust,
Trimmings, &
Other Finishing
Wastes
LW - Liquid Wastes
- Solid Wastes

Source: Adapted from Conrad et al. (1976)

Figure 5-1. A general process flow diagram illustrating tannery inputs and wastestreams.

TABLE 5-6. ESTIMATED LOSSES OF BISAZOBIPHENYL DYES IN THE LEATHER INDUSTRY

	Quantity (1,000 lb)[a/]			
Loss source	1975	1976	1977	1978
Total dye consumption[b/]	531-870	691-1,183	754-1,163	863-1,390
Processing losses (10-20% of consumption)[c/]				
Solid waste (99.8%)	53-174	69-236	75-232	86-277
Liquid waste (~0.1%)	~0.1-0.2	~0.1-0.2	~0.1-0.2	~0.1-0.3
Aerosol waste (~0.1%)	~0.1-0.2	~0.1-0.2	~0.1-0.2	~0.1-0.3
Total	53-174	69-236	75-232	86-278
Total quantity of dye on finished leather	357-817	455-1,114	522-1,088	585-1,304

a/ Based on 100% BAB dye; not standardized commercial dye.

b/ Taken from Table 5-3.

c/ The 10-20% loss range was derived from average dye uptake percentage (Radding et al., 1978) and an MRI estimation of additional processing losses.

SECTION 6

PAPER INDUSTRY

INDUSTRY OVERVIEW

The paper industry* is a very large, diversified industry. The American Paper Institute has over 200 member companies, who together represent approximately 90% of domestic paper and paperboard production. The industry is not dominated by a few large companies; the biggest single U.S. paper and paperboard producer turns out less than 10% of total production. In order to account for 50% of the total U.S. production, the production of 50 or more companies would have to be included (Bognar, 1979).

The expense of transporting low cost paper goods great distances prior to sale is not cost-effective. Consequently, paper mills are scattered across the country and are located wherever there is sufficient wood fiber and processing water. The northeast, north central, southern, and northwestern states all support significant levels of paper and paperboard production (Vogt, 1974).

At various mills, different tree species are harvested for pulp, different types and amounts of recycled paper are included in processing, and different mechanical and chemical methods are employed (note Table 6-1). Some companies are small; others are large corporations or subsidiaries thereof. Thousands of different end products are provided by the diverse segments of the industry.

Table 6-2 enumerates paper and paperboard production for the 1975 through 1978 period. The following 10 end use categories are listed (Franklin et al., 1979):

Newsprint - A generic term used to describe paper of the type generally used in the publication of newspapers. The furnish** is largely mechanical (ground wood) pulp, along with some chemical wood pulp.

Printing and Writing Paper - Printing papers are those papers utilized by the printing industry for mass communications and other end uses where a multitude of copies are required

---

* General references to the "paper" industry include the closely associated paperboard industry.

** The "furnish" is the fiber-water slurry which receives the dye.

TABLE 6-1. ORIGIN AND USE OF VARIOUS WOOD PULP

Type	Process	Wood	End uses
Unbleached	Ground wood	Balsam/spruce	Newsprint; board
Bleached	Mechanical Thermo-mechanical	Balsam/spruce	Paper; paperboard; foodboard
Unbleached sulphate (Kraft)	Chemical	Pine/spruce/hemlock/fir	Paper; paperboard; towels; tissue; linerboard
Bleached sulphate	Chemical	Pine/spruce/hemlock/fir	Fine papers; tissues; toweling; board; paper
Unbleached sulphite	Chemical	Pine/spruce/hemlock/fir	Fine papers; tissues; toweling; board; paper
Bleached sulphite	Chemical	Pine/spruce/hemlock/fir	Fine papers; tissues; toweling; board; paper
Soda pulp	Chemical	Cottonwood/maple/poplar/gum/etc.	Extender for white papers; tissues; toweling
Semichemical	-	Secondary fibers (recycled material)	Corrugating medium; linerboard

Source: Adapted from Continental Forest Industries, Inc. (1978).

TABLE 6-2. PAPER PRODUCTION BY END USE, 1975 TO 1978

	Production quantity (10^6 short tons)			
	1975	1976	1977	1978
Paper				
Newsprint	3.7	3.7	3.9	3.8
Printing and writing paper	11.0	13.2	13.8	14.5
Packaging paper	4.2	4.9	4.9	4.9
Special industrial papers	0.4	0.6	0.5	0.5
Tissue paper	4.0	4.2	4.3	4.2
Total	23.3	26.6	27.4	27.9
Paperboard				
Container board	17.4	19.9	20.4	21.5
Boxboard	7.4	8.6	8.5	8.8
Total	24.8	28.5	28.9	30.3
Other				
Building paper	1.6	1.8	1.7	2.0
Insulating and hard pressed board	3.0	3.6	3.8	3.6
Wet machine board	0.1	0.1	0.1	0.1
Total	4.7	5.5	5.6	5.7
Grand total	52.8	60.6	61.9	63.9

Sources: Data for 1975 through 1977 taken from Franklin et al., 1979. Data for 1978 taken from Funaroff, 1979.

generally by long press runs on high speed equipment. Printing papers (such as offset, book paper, and ground wood printing paper) are frequently printed on both sides. Therefore, opacity is generally important for products such as magazines, books, pamphlets, and greeting cards, etc. This paper is made in a wide range of qualities from chemical and mechanical wood pulp and, in some products, with a cotton fiber pulp content. Printing paper may be coated or uncoated.

Writing paper consists of a variety of papers (bond, ledger, manifold, etc.) suitable for pencil, pen and ink, or for use with a typewriter, automatic accounting equipment, computer, etc. The majority of the writing paper is made from chemical wood pulp. Cotton fiber pulps are used in about 5% of the tonnage. In addition, mechanical wood pulps may be used in some instances. The papers are usually uncoated but may be coated for use in specialized end uses.

Packaging Paper - Wrapping paper; shipping sack; bag and sack other than shipping sack; and other converting papers 18 lb* and over.

Special Industrial Papers - Paper and board of all weights, calipers (thickness), and finishes designed for specialized end uses, such as abrasive paper, absorbent paper, cable paper, electrical insulation, vulcanized fiber, and resin-impregnating.

Tissue Paper - A general term indicating a class of papers of characteristic gauzy texture, in some cases fairly transparent, made in weights lighter than 18 lb.* The class includes sanitary tissues, e.g., toilet paper, wrapping tissue, towels, napkins, facial tissues, and wipers.

Containerboard - A general term designating: (a) the component materials used in the fabrication of corrugated paperboard and solid fiber paperboard--linerboard, corrugating medium, chipboard; and (b) solid fiber or corrugated combined paperboard used in the manufacture of shipping containers and related products.

Boxboard - A general term designating the paperboard used in fabricating folding cartons, setup boxes, milk cartons, and foodboard. It may be made of wood pulp or waste paper or any combinations of these and may be plain, lined, or clay coated.

Building Paper - Sheathing paper, felts (roofing, floor covering, automotive, deadening, industrial pipe covering, refrigeration), asbestos paper and asbestos-filled paper, flexible wood fiber insulation.

---

* Grading of paper by pound refers to the weight of product per ream, i.e., one 3,000 sq ft ream, or every 500 sheets measuring 24 x 36 in. per sheet, of "18 lb" paper weights 18 lb.

Insulating and Hard Pressed Board - A group of paper and paperboard products used in making insulating boards and construction panels. A fibrous-felted homogeneous panel made by interfelting of the fibers, e.g., interior building board, wallboard, sound deadening board, acoustical tile, exterior sheathing board, roof insulation board, trailer board, etc.

Wet Machine Board - Binders board, shoe board (e.g., counter board, heel board, and innersole), automotive board, chair seat backing, coaster board, luggage, mill board, panel board, table top board, etc. (Franklin et al., 1979).

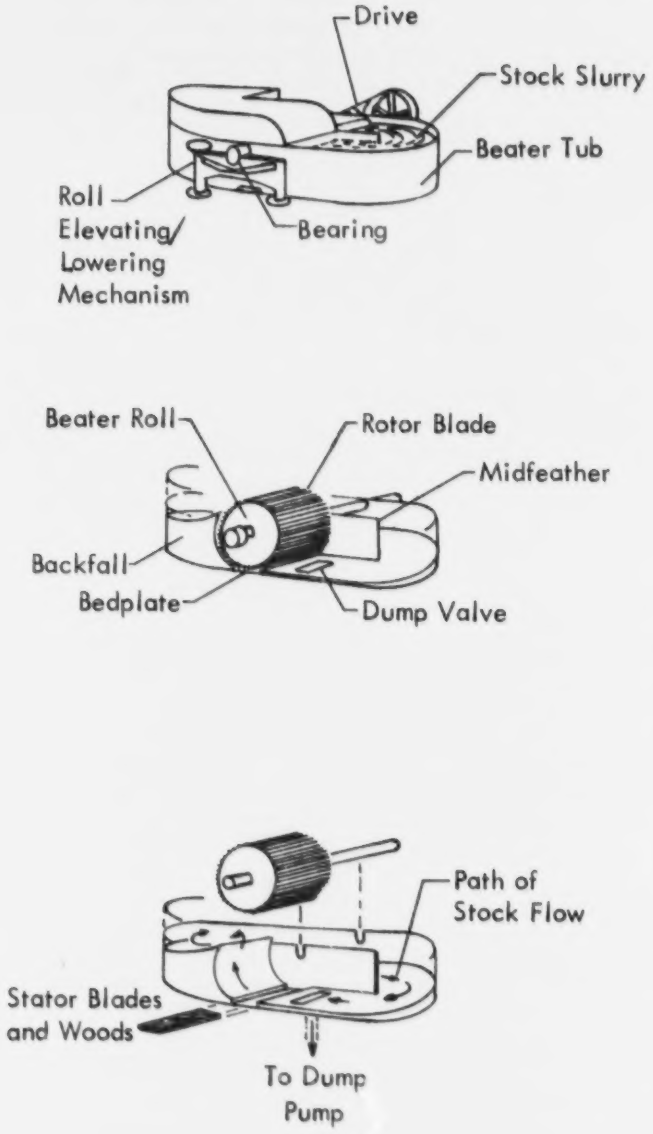
PAPER PROCESSING AND DYEING

Though the equipment may vary, over 90% of all colored paper is dyed in the same manner. The fiber is dyed prior to its aggregation into sheets while it is in an aqueous bath (Cramsie, 1979).

In one common approach, the dyeing takes place in the beater (note Figure 6-1). As the name implies, the beater is designed to fragment fiber bundles and shorten individual fibers in the pulp. A typical beater has the appearance of an oval-shaped tank. A divider in the center of the tank produces an oblong channel. The floor of this channel slopes downward from a backfall immediately behind the beater roll which is suspended across one side of the oblong channel. The beater roll has a series of longitudinal blades. As the roll turns, these blades beat the pulp against stationary blades beneath the roll. The rotating blades also force the slurry to circulate continuously around the tank. After the appropriate preparation of the fiber, as determined by the nature of the original stock and the type of end product desired, various papermaking compounds including dye may be added to the slurry in the beater (Danforth, 1970).

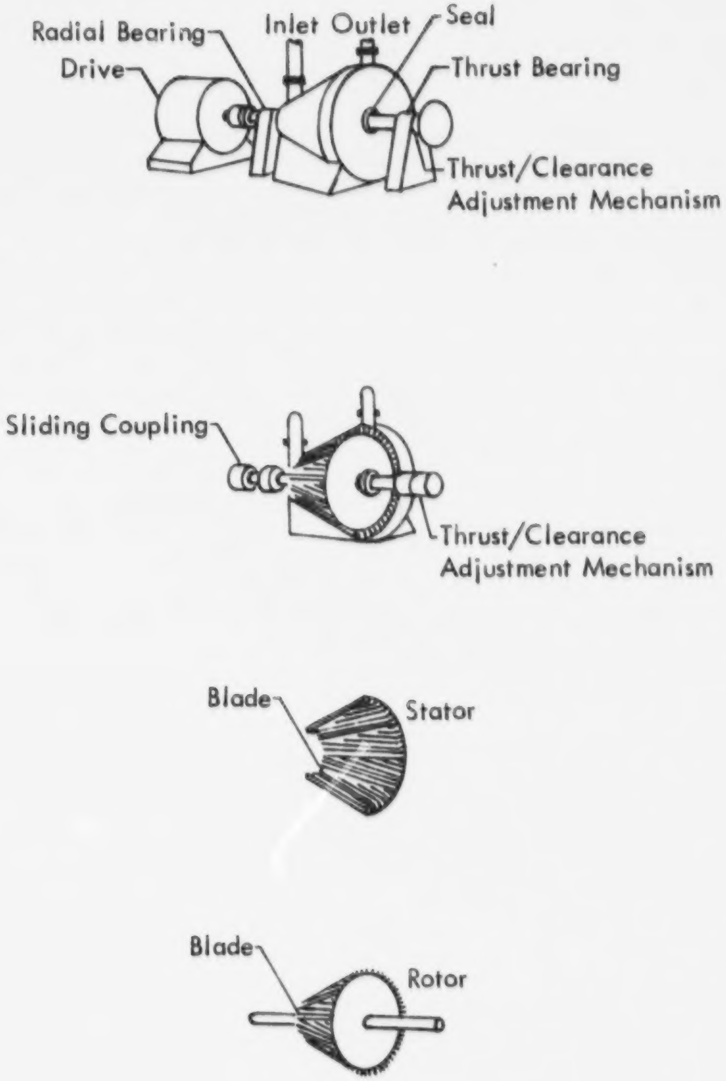
The main alternative to the traditional beater consists of two or three separate machines--a pulper, which defibers the dry pulp and/or paper in a water medium; a continuous refiner, in which the various papermaking materials are added to the furnish; and occasionally, a deflaker added between the pulper and refiner. The deflaker ensures the reduction of pulp to individual fibers after the slurry leaves the pulper and before it is fed into the refiner. (Any remaining flakes of wood or paper are destroyed while the stock passes through the deflaker.

Though the design details may vary considerably, all three of these machines consist of containment vessels with rotating and stationary blades. The purported advantages of the continuous refining technology, compared to the use of beaters, include the greater ease with which pulpers recycle unsaleable paper (sometimes referred to as "broke") and other materials which are hard to defiber; adaptability to automated production; and more efficient, continuous operation, since dye color changes can be accomplished more easily and more rapidly (Danforth, 1970; Landerl, 1979). One example of a continuous paper refiner is a conical refiner shown in Figure 6-2.


Drive
Stock Slurry
Beater Tub
Roll Elevating/ Lowering Mechanism
Bearing
Beater Roll
Rotor Blade
Midfeather
Backfall
Bedplate
Dump Valve
Path of Stock Flow
Stator Blades and Woods
To Dump Pump

Source: Adapted from Danforth (1970).

Figure 6-1. Simplified representation of a beater.


Radial Bearing
Inlet
Outlet
Seal
Drive
Thrust Bearing
Thrust/Clearance Adjustment Mechanism
Sliding Coupling
Thrust/Clearance Adjustment Mechanism
Blade
Stator
Blade
Rotor

Source: Adapted from Danforth (1970).

Figure 6-2. Simplified representation of a conical continuous refiner.

Regardless of how the pulp is reduced to the proper consistency, dye is commonly added to the beater or continuous refiner after the mechanical breakdown of the fiber has progressed to the appropriate stage for the given application. The dye may be added as a liquid solution or as a dry powder.

The most important group of dyes used in the coloring of paper is the direct dye. The affinity of these dyes for cellulose fiber makes them more versatile and more easy to control than either the acid or the basic dyes (Lips, 1970).

Because direct dyes are not very soluble, they are generally limited to less than a 1% aqueous solution. However, the ability to dye fiber directly allows effective coloring to take place despite these low concentrations. This affinity for cellulose fiber also makes direct dye a logical choice for the coloring of facial tissue, toilet tissue, and absorbent tissues where size* and alum are not used (acid dye could not be used under these circumstances).

The two primary limitations of the direct dyes are a lack of brilliance and the tendency to unevenly dye the paper if used improperly. This latter problem refers to a difficulty caused by the rapid exhaustion of dye on only a portion of the fiber being dyed. When this occurs, the paper product does not possess a uniform color but is speckled because the paper is composed of both deeply dyed fiber and uncolored fiber. Some direct dyes are much more prone towards this problem than others. The remedy lies in the use of cool, dilute dye solutions (Lips, 1970).

The dominance of direct dyes in paper coloring applications may be explained by the deficiencies of the competing dye classes.

Acid dyes are much more soluble than direct dyes; some exhibit solubilities over 10%. However, acid dyes have very little attraction for the cellulose fiber. As a result, it is easy to achieve a high concentration of color in the fiber slurry but difficult to join the color to the fiber. When acid dyes are used on paper, the color is usually retained in the sheet by a chemical complex formed between alum and rosin size. Sometimes other retention aids are also employed. As noted previously, this situation precludes the use of acid dyes in tissues and absorbent applications. Acid dyed products are also unsuitable for uses involving direct contact with moist or wet foods because the highly soluble dye tends to migrate (Lips, 1970).

Although most paper is dyed using the technology just described, some surface coloring also takes place after the paper sheet is formed. In these cases, dye may be added to the product via water boxes at the calendar stack or via the surface sizing solution at the size press. The colorants used are predominantly fluorescent white dyes and various acid dyes (Lips, 1970).

---

* Size refers to finely ground additives (i.e., rosin, paraffin, wax) which intermingle with the fiber in the production of water-resistant papers.

Because these applications are minor with respect to total dye consumption and because no appreciable quantity of benzidine-related dyes is thought to be involved in such usage, no detailed discussion of surface coloring or coating will be undertaken (Lips, 1970).

DYE CONSUMPTION

Color is an important sales tool in the paper industry. As such, the details of dye utilization are proprietary. Despite this information barrier, some generalizations can be made in regard to dye usage per unit of production (see Table 6-3).

TABLE 6-3. COMMERCIAL DYE USAGE IN PAPER AND PAPERBOARD

Dye Consumption[a]	Representative products
0-0.5 lb/short ton	Unbleached kraft products (brown grocery bags, wrapping paper, and cardboard boxes); white paperboard for food packaging; white papers; white tissues
0.5-2 lb/short ton	Household tissue, paper towels, and paper napkins
2-60 lb/short ton	Miscellaneous uses such as construction paper, wrapping paper, writing paper.
60-80 lb/short ton	Full shade tissues and brightly colored glassine

[a] MRI estimates derived principally from contacts with Cramsie (1979, Landerl (1979), and Kasprzak (1979). These levels represent commercial dyes, not active dye.

At the lower end of the range where dye consumption is less than 0.5 lb/ short ton, dye is used to slightly modify existing colors (Landerl, 1979; Cramsie, 1979). For example, small additions of brown color may be employed to tint unbleached kraft for grocery bags or to match the color of recycled fibers with the unbleached kraft in such products. In the manufacture of white paper or paperboard, reddish-blue is added to tint away a yellowish cast present in the bleached pulps.

In the intermediate range, 0.5 lb to 2 lb/short ton of product, dye is employed to impart color to many different products, such as paper towels, tissues, and stationery.

At the upper end of the range where consumption is as high as 80 lb/ short ton, dye applications yield maximum color intensities. The products which commonly receive this level of colorant addition include full shade tissues and brightly colored glassine (Landerl, 1979; Cramsie, 1979; and Kasprzak, 1979).

No data were found which allow a quantification of general dye consumption or bisazobiphenyl (BAB) dye consumption in the paper industry. In the absence of authoritative information, the estimates in Tables 3-9 and 3-14 were used as approximations of the level of consumption by paper and paperboard producers of the dyes of interest to this study. These estimated consumption quantities are shown in Table 6-4. Consumption quantities derived by Jenkins (1978) provide a considerably higher estimate of BAB dyes in the paper industry.

Direct dyes have been the most important class of dyes used in the paper industry (Lips, 1970). As previously noted in the discussion of paper dyeing technology, direct dyes are particularly suited to the job of coloring tissues and other absorbent papers. Full shade tissue and other absorbent paper (highly colored glassine) requires a much higher level of dye application per weight of product than any other category of production (Landerl, 1979; Cramsie, 1979).

In addition to the coloration of tissues, another large use of dye by the paper industry is the tinting of white paper. In order to yield a white paper, blues and reds are commonly added to remove the yellow color present in papermaking fiber. 3,3'-Dimethoxybenzidine-based and other direct blues receive significant use in this area (Landerl, 1979). Though tinting white paper represents a low usage per ton, total production of white paper represents a very large volume (Lips, 1970).

ESTIMATED LOSSES

The discussion which follows presents an estimation of the total quantity of BAB dye which remains a part of finished paper and paperboard products, and also the quantity that becomes a constituent of processing waste streams. The calculations required to quantify dye uptake are taken from comments by Landerl (1979). This source indicated that about 90 to 98% of the dye employed for the coloring of paper is successfully joined to the papermaking materials. In order to allow for losses of dyed furnish and size, trimmings,

TABLE 6-4. ESTIMATED CONSUMPTION OF BAB DYES BY THE PAPER INDUSTRY

Dye base	1975		1976		1977		1978	
	(10^3 lb)[a]	%	(10^3 lb)	%	(10^3 lb)	%	(10^3 lb)	%
BEN[b]	460-725	~62	775-1,230	~73	540-825	~56	85-105	~12
DMOB[c]	308-368	~37	308-414	~26	441-550	~42	540-825	~86
DMB[d]	11-27	~1	11-27	~1	16-30	~2	18-22	~2
Total	779-1,120		1,094-1,671		997-1,405		643-952	

[a] Quantities of dyes estimated from Tables 3-8 and 3-9; quantities in terms of active dye (100% dye).

[b] Dyes based on benzidine

[c] Dyes based on 3,3'-dimethoxybenzidine

[d] Dyes based on 3,3'-dimethylbenzidine

and other miscellaneous losses during production, this range is lowered to 85 to 95% for a calculation of BAB dye retention on finished paper and paperboard products.

The remaining 5 to 15% of the dye consumed in processing necessarily enters production waste streams (note Figure 6-3). No definitive information is available to provide a quantitative breakdown for the fate of waste dyestuffs in paper mills. However, some relevant facts are known. The dyes in question have a strong affinity for cellulose fiber (Lips, 1970). There is sufficient fiber and size in the whitewater system to absorb and/or adsorb the vast majority of the dye (especially, direct dye) employed. The direct dye formulations used in the paper industry are not highly soluble in water (Lips, 1970). Volatile losses during the mixing of dyes and the drying of dyed paper may account for a minor loss of BAB material, but no evidence is available which quantifies these losses. Many modern mills rely on premixed liquid dye formulations which are automatically metered into processing equipment (Lips, 1970; Landerl, 1979). Changeovers to this production methodology have been encouraged because of industrial hygiene considerations. One of the results of such processing changes is a decline in volatile and airborne particulate wastes from dye mixing.

All of this evidence indicates that the majority of the BAB dye that is lost during processing ultimately becomes solid waste--either as a component of wastewater sludge, trimmings, plant dust, or other miscellaneous residues. Additional losses as solid waste will occur from trimmings resulting from industrial fabrication of specific paper products.

Consequently, the fate of the BAB dyes lost during the coloring of paper and paperboard, which represents ~ 5 to 15% of consumption, is thought to be greater than 99.8% solid waste, less than 0.1% liquid waste, and less than 0.1% volatile waste. Table 6-5 summarizes the estimated losses for these dyes in the paper and paperboard industry during 1975 through 1978.

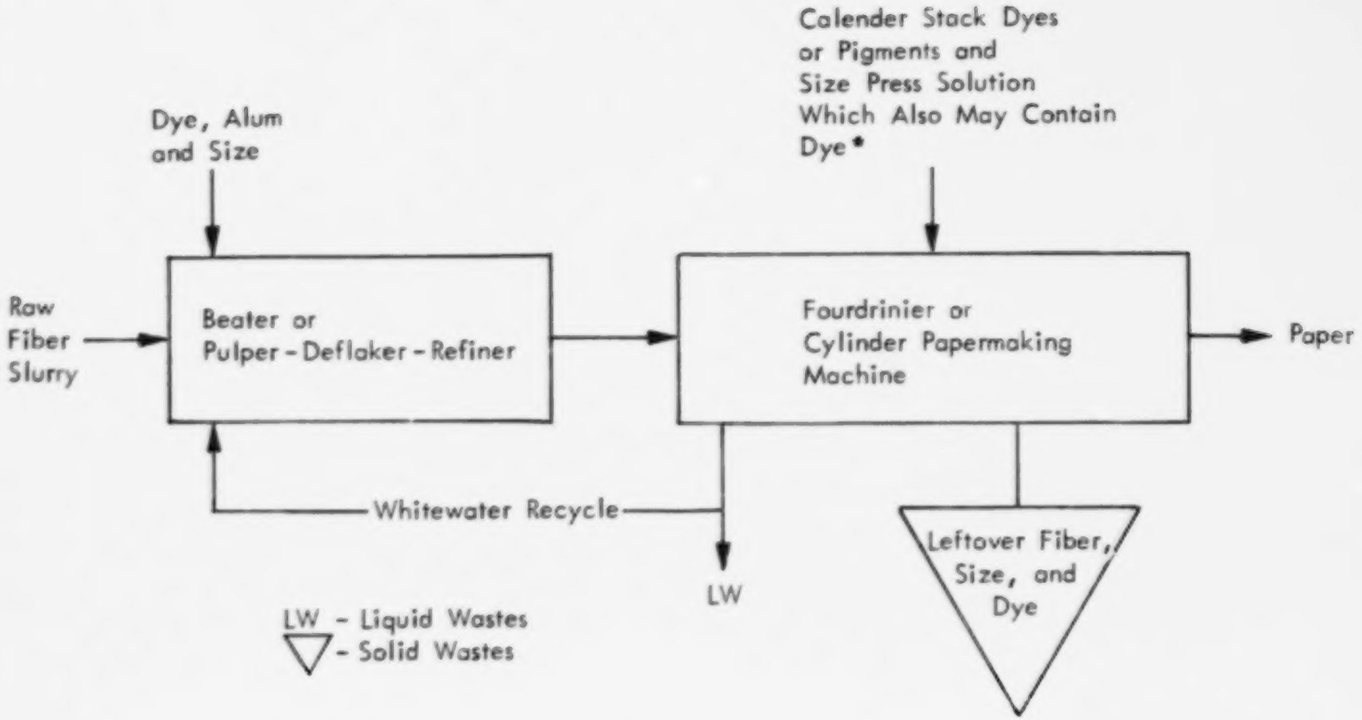
TABLE 6-5. SUMMARY OF ESTIMATED BISAZOBIPHENYL DYE LOSSES FROM THE PAPER INDUSTRY

Loss Source	Quantity (1,000 lb)			
	1975	1976	1977	1978
Total BAB dye consumption a/	779-1,120	1,094-1,671	997-1,405	643-952
Dye loss during processing:				
Solid waste (~99.8%)	39-168	55-250	50-210	32-142
Water waste (~0.1%) b/	~ 0.1-0.2	0.1-0.3	0.1-0.2	~ 0.1
Volatile waste (~0.1%) b/	~ 0.1-0.2	0.1-0.3	0.1-0.2	~0.1
Total loss (~5-15% of total dye consumption) c/	39-168	55-251	50-210	32-142
Dye remaining in finished paper product	611-1,081	843-1,616	787-1,355	501-920

a/ Quantities are 100% dye; not standardized commercial dyes (see Table 6-4).

b/ MRI estimates

c/ The total percentage of dye loss was derived from information from Landerl (1979) and an MRI estimation to allow for additional processing losses.


Calender Stack Dyes
or Pigments and
Size Press Solution
Which Also May Contain
Dye*
Dye, Alum
and Size
Raw
Fiber
Slurry
Beater or
Pulper - Deflaker - Refiner
Fourdrinier or
Cylinder Papermaking
Machine
Paper
Whitewater Recycle
LW
Leftover Fiber,
Size, and
Dye
LW - Liquid Wastes
▽ - Solid Wastes

* Addition of dye at this point is not the most common practice. The colorants used are predominantly fluorescent white dyes and various acid dyes (Lips, 1970). No significant consumption of benzidine-related material is thought to occur here.

Figure 6-3. A general process flow diagram illustrating papermaking inputs and wastestreams.

SECTION 7

PIGMENT PRODUCTION

This section discusses the manufacturing process for diarylide pigments, sources of loss during production and approximate magnitudes of those losses, published and estimated production quantities, and usage patterns for each of the pigments.

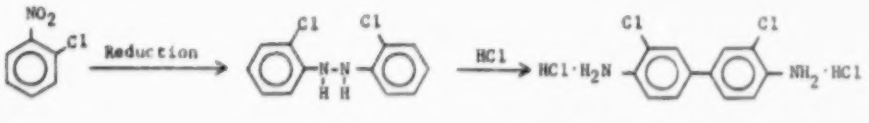
MANUFACTURING PROCESS

The manufacturing process consists of two parts: the production of 3,3'-dichlorobenzidine and 3,3'-dimethoxybenzidine and the production of the various pigments. For pigments based upon 3,3'-dichlorobenzidine, the dihydrochloride salt is used as the starting material. For pigments based upon 3,3'-dimethoxybenzidine, either the dihydrochloride salt or the free base may be utilized. No pigments based on 3,3'-dimethylbenzidine are commercially produced in the United States at the present time.

3,3'-Dichlorobenzidine Manufacture

The commercial scale production of 3,3'-dichlorobenzidine proceeds by the reduction of o-nitrochlorobenzene followed by acid rearrangement of the resulting dichlorohydrazobenzene to the desired product (Powell et al., 1979).

Both of the current U.S. producers of dichlorobenzidine (Bofors Lakeway and Upjohn) employ the o-nitrochlorobenzene reduction process followed by rearrangement with acid, usually hydrochloric (Wolthuis, 1979). The reaction for the 3,3'-dichlorobenzidine production is shown is Equation 7-1. Both U.S. manufacturers employ a batch process with dedicated equipment. Following the reduction step, the dichlorohydrazobenzene solution may be purified prior to acid rearrangement. The purified solution is treated with acid to produce a solution containing approximately 80 to 85% crude 3,3'-dichlorobenzidine and 15 to 20% other rearrangement products resulting from coupling of the rings in positions other than the desired one. The rearrangement products are removed by proprietary purification processes (no further details were



(7-1)

available). Approximately 0.5 to 1% dichlorobenzidine dihydrochloride is included in the "acid" stream containing the rearrangement products. This stream is "treated" to reduce dichlorobenzidine levels, and the solid wastes are transported to an EPA-approved site by a licensed hauler (Wolthuis, 1979; DCMA, 1980).

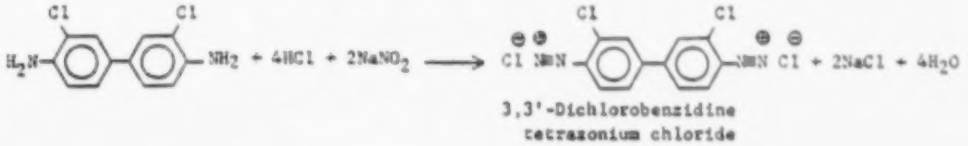
The purified dichlorobenzidine is isolated as the dihydrochloride salt by being either filtered or centrifuged. One manufacturer estimated that 0.5 to 1.5% dichlorobenzidine would be contained in the wastestream following isolation of the solid dichlorobenzidine dihydrochloride. At Bofors Lakeway, the wastestream from the isolation procedure is transferred to a recycle system, which results in a concentration of the waste stream (Wolthuis, 1979). This concentrated waste stream is then recycled into the process. Periodically, the waste stream is purged and the aqueous waste removed to an EPA-approved disposal site. The other producer sends the wastestream from the isolation of the solid dichlorobenzidine dihydrochloride to biological wastewater treatment facilities.

The dichlorobenzidine dihydrochloride is transferred directly into drums for shipment or storage. Because the product is shipped as a damp material, minimal losses should occur in the form of dust. Since the entire production process at each manufacturer utilizes dedicated equipment, dichlorobenzidine dihydrochloride remaining in equipment such as blenders and packaging machines is incorporated into the next batch of product.

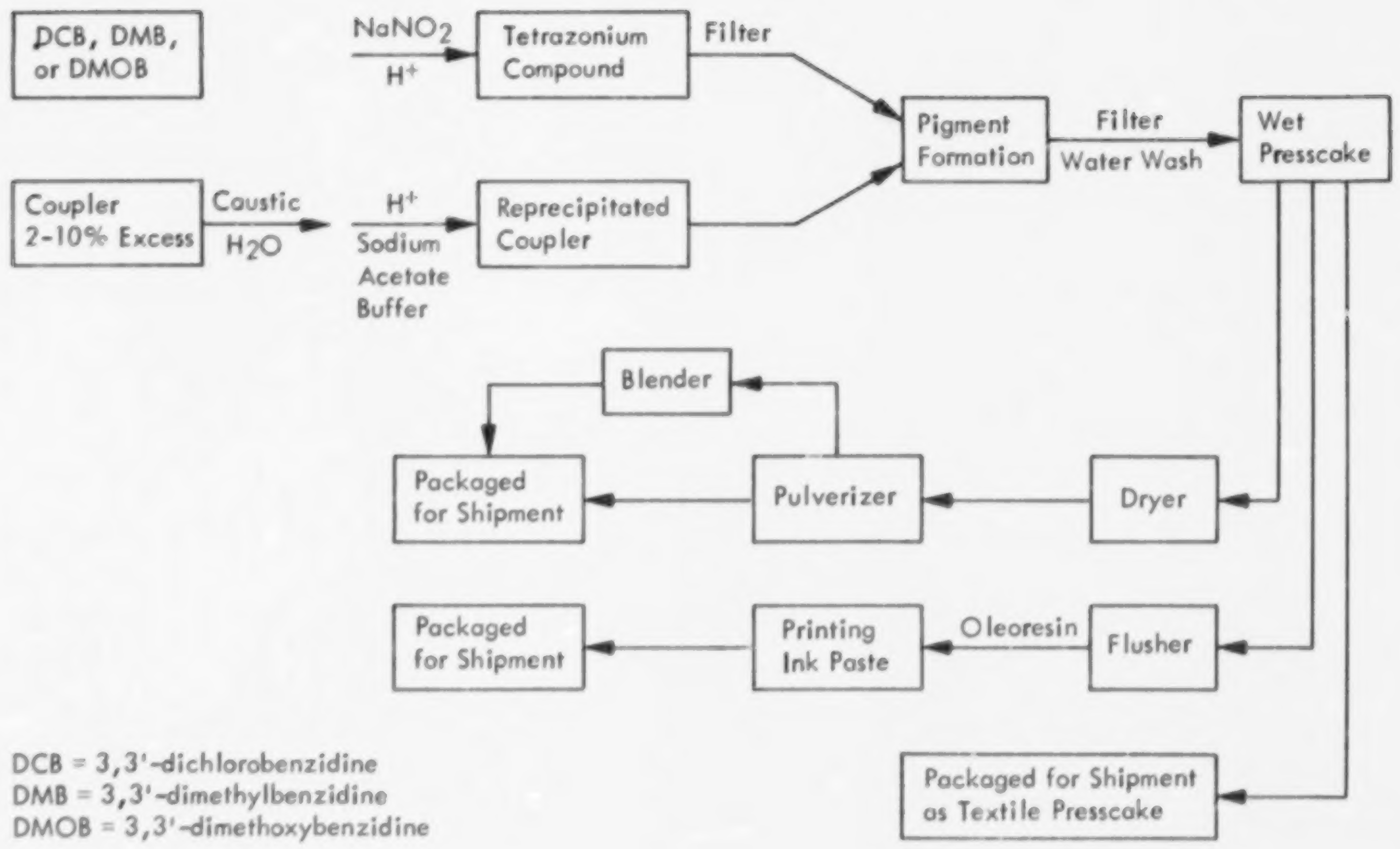
Pigment Manufacture

A basic flow diagram for the manufacture and processing of pigments produced from 3,3'-dichlorobenzidine, 3,3'-dimethylbenzidine (tolidine), or 3,3'-dimethoxybenzidine (dianisidine) is shown in Figure 7-1.

For 3,3'-dichlorobenzidine, the formation of the tetrazonium compound would be as shown in Equation 7-2. The dichlorobenzidine dihydrochloride is received as a damp or moist powder containing about 10% water. It is slurried with water and additional hydrochloric acid, cooled by the addition of ice, and treated with sodium nitrite to form the water-soluble tetrazonium compound. Although a filtration step is included in Figure 7-1, industry sources state that, as a rule, the tetrazonium compound is not filtered. If the tetrazonium solution appears to require clarification, then the filtration step would be performed. Losses resulting from filtration were estimated by industry to be approximately 0.1 to 0.3%. The filter contains some form of filter aid which would likely be discarded as solid waste after treatment with sodium hypochlorite or other decontaminating agent.



(7-2)


DCB, DMB, or DMOB
Coupler 2-10% Excess
Caustic
H_2O
$NaNO_2$
H^+
Tetrazonium Compound
H^+
Sodium Acetate Buffer
Reprecipitated Coupler
Filter
Pigment Formation
Filter
Water Wash
Wet Presscake
Blender
Packaged for Shipment
Pulverizer
Dryer
Packaged for Shipment
Printing Ink Paste
Oleoresin
Flusher
Packaged for Shipment as Textile Presscake

DCB = 3,3'-dichlorobenzidine
DMB = 3,3'-dimethylbenzidine
DMOB = 3,3'-dimethoxybenzidine

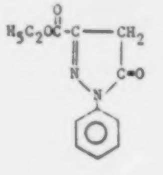
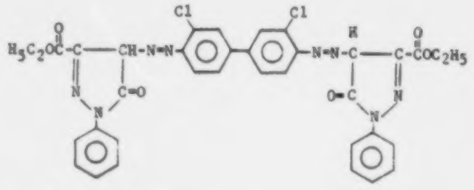
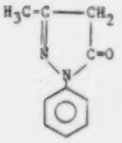
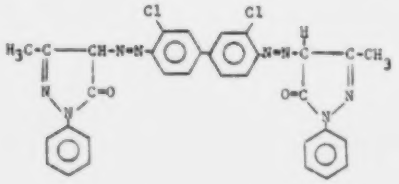
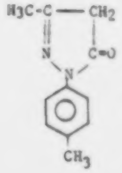
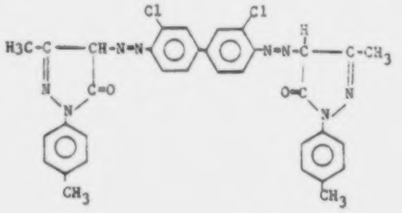
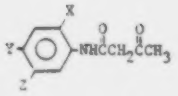
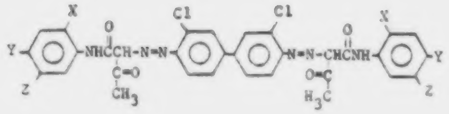
Figure 7-1. General flow diagram for pigment manufacture.

Pigment formation occurs upon mixing of a 2 to 10% excess of the coupler and an aqueous solution of the tetrazonium compound. Table 7-1 shows the couplers and structures of the dyes of interest to this report. Prior to pigment formation, the coupler may be reprecipitated in a finely divided form and a buffer added to maintain the pH within the range necessary for completion of the coupling reaction and to ensure proper color characteristics. The tetrazonium solution and the coupler slurry are mixed and pigment formation is initiated. The resultant pigments are insoluble in aqueous solution and precipitate upon formation. Industry sources state that the reaction proceeds to basically 100% of the theoretical yield and that losses resulting from the pigment manufacture are very small. MRI feels it is probable that a small amount (0.5 to 1.0%) of dichlorobenzidine tetrazonium chloride or water soluble by-products remains in solution during pigment manufacture. The pigment is then filtered and washed with water; the solid pigment remaining on the filter is termed the presscake. Industry sources state that the presscake remaining after the final water wash contains approximately 20 ppm or less of the dihydrochloride salt of dichlorobenzidine, dimethylbenzidine, or dimethoxybenzidine. Because the levels adsorbed on the pigments are low, subsequent discussions in this subsection concerning process losses will refer to losses of pigment and will not consider the 20 ppm or less of the adsorbed acid salt of dichlorobenzidine, dimethylbenzidine, or dimethoxybenzidine.

The presscake can be treated in three ways depending upon the final use for the particular pigment: "flushed color," dry pigment, or presscake. If a flushed color is to be produced, the presscake is transferred from the filter to a unit called a flusher. In the flusher, an oleoresinous material is added and the pigment dispersed in the vehicle to form a wet, sticky paste to be used for lithographic purposes. The flushed color is then transferred to shipping or storage containers. Pigment manufacturers estimated that handling losses would be approximately 1 to 3%; these losses would occur primarily in the transfer of the presscake to the flusher and from the flusher to the shipment or storage containers.

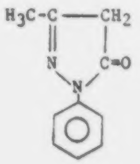
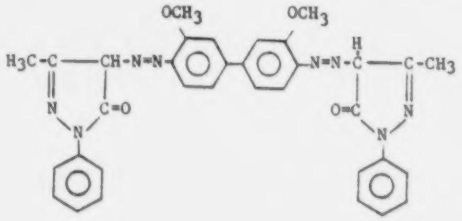
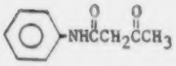
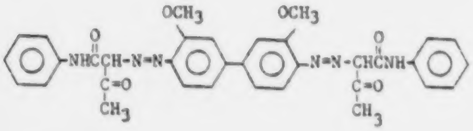
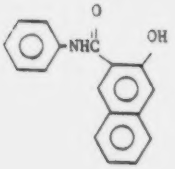
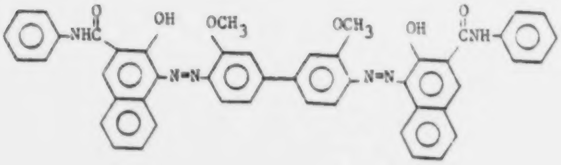
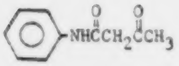
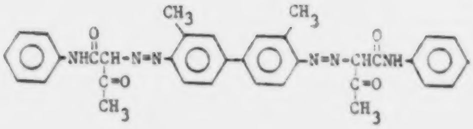
If the pigment is to be shipped or stored as a dry powder, the wet presscake is transferred to a drier. Depending on the volume of the pigment to be produced, the drying process may be batch or continuous with or without dedicated equipment. From the drier, the dry presscake is pulverized and/or blended to produce the finished pigment which is then packaged in drums or bags for shipment or storage in a warehouse. Finely divided dry pigment as dust from the pulverizer is vented to a baghouse for collection. Attempts are made to reclaim as much pigment as possible from the baghouse filters and the recovered pigment is blended into another batch. Very finely divided particles, or "fines," remaining in the filters are discarded as solid waste. Overall losses of pigment resulting from the processing of the dry pigment are estimated by a major pigment manufacturer to be approximately 1 to 3%, the principal sources being the pulverizing operation and the various transfer operations from machines to containers. The pulverizing step is estimated by MRI to be the largest single loss source, accounting for approximately 50% of the pigment losses resulting from the handling of the dry pigments. If the equipment, such as driers and pulverizers, is dedicated for the specific pigment, little, if any, cleaning of the equipment would occur and losses

TABLE 7-1. STRUCTURES OF SELECTED DIARYLIDE PIGMENTS

Pigment	Coupler	Structure
DCB[a] based		
Red 38 MW = 739.6		
Orange 13 MW = 623.5		
Orange 34 MW = 651.5		
Yellow pigments		

Yellow 12	X = H;	Y = H;	Z = H	MW = 629.4
Yellow 13	X = CH_3;	Y = CH_3;	Z = H	MW = 685.6
Yellow 14	X = CH_3;	Y = H;	Z = H	MW = 657.4
Yellow 17	X = OCH_3;	Y = H;	Z = H	MW = 689.4
Yellow 55	X = H;	Y = CH_3;	Z = H	MW = 657.5
Yellow 83	X = OCH_3;	Y = Cl;	Z = OCH_3	MW = 820.5

TABLE 7-1. (concluded)

Pigment	Coupler	Structure
DMOB[b] based		
Red 41 MW = 642.7		
Orange 16 MW = 620.6		
Blue 25 MW = 792.8		
DMB[c] based		
Orange 15 MW = 588.6		

---

a/ DCB = 3,3'-dichlorobenzidine; MW = 253.13

b/ DMOB = 3,3'-dimethoxybenzidine; MW = 244.29

c/ DMB = 3,3'-dimethylbenzidine; MW = 212.28

from this source would be extremely small. Additionally, if a light-colored pigment (e.g., yellow) were to be followed by a dark pigment (e.g., blue or red), the equipment would generally not be cleaned prior to changing pigments since the incorporation of a small amount of light-colored pigment into a dark shade would have little effect on the overall dark color. The same would not be true, however, for the reverse situation in which a light shade followed a dark shade. In these instances, the equipment would likely be cleaned prior to use with the lighter colored pigment. If cleaning is required, MRI estimates that pigment losses could be 0.5 to 1%.

On occasion, an off-standard shade of dry pigment may be produced. If the shade is darker than the standard or specified color, an extender (e.g., barium sulfate) is used as an inert diluent to reduce the color intensity to the specified level. If the shade is lighter than the standard or specified color, it is blended with a quantity of darker than standard pigment to produce the correct color. When the blending operation is used and cleaning of the blender is required, industry sources state that losses would be less than 1%.

The third method of pigment processing is for presscake. For use in textile printing or water-based paint, ink, or coatings, the pigment is shipped in the water-wet form of the presscake, which has a dough-like consistency, or as a dispersed slurry. The only losses would result from the mechanical transfer of the presscake or the slurry from the filter to drums for shipment. As with the transfer in the formation of flushed colors, losses resulting from removal of the pigment from the filter could be approximately 0.5 to 1%.

PRODUCTION HISTORY

The pigments considered in this study were delineated earlier in Table 7-1. Except for the inclusion of pigment Yellow 83, this listing is virtually the same as those considered in a previous report (Powell et al., 1979). Manufacturers of each of the pigments are presented in Table 7-2 for the period 1975 to 1978. Within this time period, numerous manufacturers of diarylide pigments have ceased production or have been sold to other companies. In 1975, 29 companies manufactured one or more pigments derived from 3,3'-dichlorobenzidine, 3,3'-dimethylbenzidine, or 3,3'-dimethoxybenzidine. Pigments Yellow 13 and 14 had the greatest number of producers, 20; followed by Yellow 12 with 19, and Yellow 17 with 18. By 1978, the total number of manufacturers had been reduced to 21. Yellow 14 was produced by the greatest number of companies, 17; followed by Yellow 17 with 15 companies. Fourteen companies manufactured Yellow 12 in 1978.

Production, sales, and import quantities of each of the pigments, as dry, full strength, 100% material, are presented in Table 7-3. For some pigments, a sufficient number of producers exist to allow a report of the production and sales data in government publications.

TABLE 7-2. PIGMENT MANUFACTURERS, 1975-1978

Producer	1975													
	Red 38	Orange 13	Orange 34	Yellow 12	Yellow 13	Yellow 14	Yellow 17	Yellow 55	Yellow 83	Red 41	Orange 16	Blue 25	Orange 15	Total produced
Allied Chemical Corporation	X	X		X		X	X			X	X		X	8
Ridgway Color and Chemical		X		X	X	X	X							5
Hercules, Inc.		X	X	X	X	X	X	X			X		X	9
Chemetron Corporation		X		X	X	X	X							5
Harshaw Chemical Company	X	X		X	X	X	X				X	X		8
Inmont Corporation	X	X	X	X	X	X	X		X		X	X		10
M. Kohnstamm and Company		X		X										2
Max Marx Color and Chemical	X	X		X	X	X	X	X		X	X			9
Ciba-Geigy	X	X	X		X	X	X	X				X		8
American Cyanamid Corporation		X		X	X	X	X							5
Harmon Color Corporation	X	X		X		X								4
Sandoz, Inc.		X		X	X		X				X	X		6
Sun Chemical Corporation	X	X		X	X	X	X		X		X	X		9
Blackman-Uhler			X		X	X	X							4
Bostik South, Inc.			X		X	X	X				X			5
United Merchants and Manufacturers			X	X	X	X	X				X			6
Sterling Drug, Inc.			X	X	X	X	X							5
Verona Division, Baychem			X		X	X	X				X			5
GAF Corporation	X				X	X					X	X		5
Paul Uhlich and Company	X									X				2
Apollo Colors, Inc.				X										1
Borden, Inc.				X										1
American Hoechst Corporation				X	X	X	X		X		X			6
E. I. du Pont				X	X	X								3
Sherwin Williams				X			X				X			3
ICI America					X									1
Crompton and Knowles					X									1
Binney and Smith, Inc.						X					X			2
Reichard-Coulston, Inc.								X						1
Total producers	9	13	8	19	20	20	18	4	3	3	14	6	2	

(continued)

TABLE 7-2. (continued)

Producer	1976													
	Red 38	Orange 13	Orange 34	Yellow 12	Yellow 13	Yellow 14	Yellow 17	Yellow 55	Yellow 83	Red 41	Orange 16	Blue 25	Orange 15	Total produced
Allied Chemical Corporation	X	X		X		X	X			X	X		X	8
Ridgway Color and Chemical		X		X	X	X								4
Hercules, Inc.		X		X	X	X	X	X			X			7
Chemetron Corporation		X		X	X	X	X		X					6
Harshaw Chemical Company	X	X		X		X	X				X			6
Inmont Corporation		X	X	X	X	X	X	X	X		X	X		10
M. Kohnstamm and Company		X												1
Max Marx Color and Chemical											X			1
Sandoz, Inc.		X				X								2
Sun Chemical Corporation				X	X	X	X		X		X			6
Blackman-Uhler			X		X	X	X							4
Bostik South, Inc.		X			X	X					X			4
United Merchants and Manufacturers			X	X	X	X	X				X			6
Sterling Drug, Inc.			X	X	X	X	X				X			6
GAF Corporation						X								1
Apollo Colors				X										1
Borden, Inc.				X		X	X							3
American Hoechst Corporation				X	X	X	X		X		X			6
Binney and Smith, Inc.						X					X			2
Keystone Color Works	X													1
Total producers	3	9	4	12	10	16	11	2	4	1	11	1	1	

(continued)

TABLE 7-2. (continued)

Producer	1977 Red 38	Orange 13	Orange 34	Yellow 12	Yellow 13	Yellow 14	Yellow 17	Yellow 55	Yellow 83	Red 41	Orange 16	Blue 25	Orange 15	Total produced
Ridgway Color and Chemical		X		X		X	X		X					5
Hercules, Inc.		X		X	X	X	X	X			X			7
Chemetron Corporation		X		X	X	X	X		X					6
Harshaw Chemical Company	X	X		X		X	X				X			6
Inmont Corporation		X	X	X		X	X	X	X		X	X		9
M. Kohnstamm and Company		X												1
Harmon Color Corporation	X	X		X		X				X	X		X	7
Sandoz, Inc.						X			X					2
Sun Chemical Corporation	X	X		X	X	X	X							6
Blackman-Uhler			X		X	X	X							4
Bostik South					X	X								2
United Merchants and Manufacturers			X	X	X	X	X				X			6
Sterling Drug			X	X	X	X	X				X			6
GAF Corporation						X								1
Apollo Colors, Inc.				X	X	X	X							4
Borden, Inc.				X		X	X							3
American Hoechst Corporation				X	X	X	X		X		X			6
Binney and Smith						X					X			2
Galaxie Chemical Corporation			X	X	X	X	X		X		X	X		8
Indol Chemical Company			X	X	X	X	X		X		X	X		8
Total producers	3	8	6	14	11	19	14	2	7	1	10	3	1	

(continued)

TABLE 7-2. (concluded)

Producer	1978 Red 38	Orange 13	Orange 34	Yellow 12	Yellow 13	Yellow 14	Yellow 17	Yellow 55	Yellow 83	Red 41	Orange 16	Blue 25	Total produced
Ridgway Color and Chemical		X		X		X	X		X				5
Hercules, Inc.		X	X	X	X	X	X	X			X		8
Chemetron Corporation		X		X	X	X	X		X				6
Harshaw Chemical	X			X		X	X				X		5
Harmon Color Corporation	X	X		X			X			X	X		6
Sandoz, Inc.		X				X			X				3
Sun Chemical Corporation		X	X	X	X	X	X		X		X		8
United Merchants and Manufacturers		X	X	X	X						X		5
Sterling Drug		X	X	X		X					X		5
Apollo Colors, Inc.				X	X	X	X						4
Borden, Inc.				X		X							2
American Hoechst Corporation				X	X	X	X		X		X		6
Binney and Smith, Inc.						X					X		2
Indol Chemical Company			X	X	X		X		X		X	X	7
Inmont Corporation		X		X	X	X	X		X		X		7
Total producers	2	9	5	13	8	12	10	1	7	1	10	1	

Sources: Synthetic Organic Chemicals, U.S. International Trade Commission, Washington, D.C., 1975-1977; Powell et al., 1979; industry contacts; MRI estimates.

TABLE 7-3. U.S. PRODUCTION AND IMPORTS OF SELECTED PIGMENTS

		Quantity (1,000 lb)			
Pigment	Source	1975	1976	1977	1978
Dichlorobenzidine-Based					
Red 38	Production[a]	[185-190][b]	141	205	[210-215]
	Sales[a]	-	-	161	-
	Import[c]	4.84	64.24	-	-
Orange 13	Production	209	267	230	237
	Sales	168	171	186	238
	Import	11.02	2.20	9.48	3.30
Orange 34	Production	99	89	75	83
	Sales	97	[89]	75	68
	Imports	-	96.47	13.42	7.7
Yellow 12	Production	6,028	7,830	8,670	11,860
	Sales	3,906	5,223	5,768	7,537
	Imports	62.12	34.65	28.71	2.26
Yellow 13	Production	240	380	367	511
	Sales	166	203	300	386
	Imports	2.56	19.98	4.63	9.66
Yellow 14	Production	1,840	3,000	3,248	3,130
	Sales	1,646	1,992	2,323	2,475
	Imports	11.06	-	0.11	5.19
Yellow 17	Production	415	767	1,002	1,370
	Sales	280	416	612	816
Yellow 55	Production	[50-60]	[50-60]	[90-110]	[140-160]
Yellow 83	Production	[600-700]	[800-900]	[900-1,100]	[1,100-1,300]
	Imports	33.22	58.39	18.99	5.78
Total Production		9,666-9,781	13,324-13,434	14,787-15,007	18,641-18,866
Total Imports		124.82	275.93	75.34	33.89

(continued)

TABLE 7-3 (concluded)

		Quantity (1,000 lb)			
Pigment	Source	1975	1976	1977	1978
Dimethylbenzidine-Based					
Orange 15	Production	[40-45]	[40-45]	[35-40]	-
	Import	-	-	-	1.19
Total Production		40-45	40-45	35-40	-
Total Imports		-	-	-	1.19
Dimethoxybenzidine-Based					
Red 41	Production	[40-60]	[40-60]	[40-60]	[40-60]
Orange 16	Production	377	475	439	465
	Sales	279	367	441	468
	Imports	-	-	2.18	-
Blue 25	Production	[170-180]	[155-165]	[145-155]	[135-145]
Total Production		587-617	670-700	624-654	640-670
Total Imports		-	-	2.18	-
Overall Totals					
Production		10,293-10,443	14,034-14,179	15,446-15,701	19,281-19,536
Imports		124.82	275.93	77.52	35.08

a/ Data from "Synthetic Organic Chemicals," U.S. International Trade Commission, Washington, D.C. 20436, 1975-1978. All quantities are in terms of dry, full strength, 100% pigment. MRI estimates the accuracy of the reported production quantities of all yellow pigments to be ± 10%; all other pigments to be ± 15%.

b/ MRI estimates are shown in brackets.

c/ Data from "Imports of Benzenoid Chemicals and Products," U.S. International Trade Commission, Washington, D.C. 20436, 1975-1978.

All other production figures were estimated by MRI based on information supplied by industry sources. These figures should be interpreted as only approximate quantities.

Opinions were solicited from pigment manufacturers regarding the accuracy of the data reported by the International Trade Commission (ITC). One manufacturer stated that in his opinion the reported data for diarylide yellows were accurate to probably ± 10% and somewhat higher for the other pigments. While other manufacturers declined to state a specific figure, opinions were that ± 10% was probably a "pretty good" estimate for the yellow pigments. For the other pigments, the opinion was that an accuracy of ± 15% is probably a fairly good representation. In 1977, production quantities of the yellow pigments accounted for over 93% of all ITC data cited in Table 7-3.

For any given year, the U.S. production quantity plus import quantity is assumed to be equal to the U.S. consumption of any specific pigment. The use of sale quantities plus imports is not employed because the sale quantity reflects only purchases by other companies and does not reflect quantities of the pigment employed for captive uses. This fact is particularly important for any pigment consumed in the printing ink industry because two of the pigment manufacturers are also the largest and second largest printing ink manufacturers in the United States. Thus, these two companies consume large quantities of pigments in captive production which are not reflected in the sales quantities of the ITC data. Industry sources indicated that, with the possible exception of some very low volume pigments, quantities of pigment committed to the warehouse for extended periods of time (years) would be a very minor factor. For the foregoing reasons, all U.S. consumption quantities of pigments employed in the succeeding sections of this report will be the sum of U.S. production plus imports.

ESTIMATED LOSSES

Losses of 3,3'-dichlorobenzidine dihydrochloride can occur during production of the material and during its use in pigment production. Data are presented in Table 7-4 for estimated losses arising solely from the manufacture of DCB, DMOB, and DMB. In Table 7-5, data are given for estimated losses of these materials during their use in pigment production. For 3,3'-dimethylbenzidine and 3,3'-dimethoxybenzidine, either the free base or the acid salt (usually the dihydrochloride) is produced and used in pigment production. The production process for 3,3'-dichlorobenzidine dihydrochloride was discussed earlier in this section. In the previous discussion, it was stated that losses of the dichlorobenzidine can occur during the purification of the crude product and during the filtration (or centrifuging) of the 3,3'-dichlorobenzidine dihydrochloride. Based on the quantities of 3,3'-dichlorobenzidine required for pigment production, estimated losses (in 1,000 lb) for the purification and filtration procedures are shown in Table 7-4. Losses of 3,3'-dimethylbenzidine and 3,3'-dimethoxybenzidine are also estimated assuming the same production procedure. Both losses receive pretreatment prior to discharge or landfill disposal.

Pigment production results in potential loss sources of raw materials, by-products, and the corresponding pigments. The estimated loss of raw materials and soluble by-products is presented in Table 7-5. Raw materials include

TABLE 7-4. ESTIMATED LOSSES OF 3,3'-DICHLOROBENZIDINE, 3,3'-DIMETHYLBENZIDINE, AND 3,3'-DIMETHOXYBENZIDINE DURING THEIR MANUFACTURE

Base	Purification losses[a] (0.5-1.0%)	Filtration losses[a] (0.5-1.5%)
3,3'-Dichlorobenzidine[b]		
1975	19-39	19-60
1976	26-55	26-83
1977	29-60	29-91
1978	37-77	39-116
3,3'-Dimethoxybenzidine[b]		
1975	1-2	1-3
1976	1-3	1-4
1977	1-2	1-4
1978	1-3	1-4
3,3'-Dimethylbenzidine[b]		
1975	0.1-0.2	0.1-0.2
1976	0.1-0.2	0.1-0.2
1977	~0.1	0.1-0.2
1978	-	-

[a] Estimated losses in terms of 1,000 lb.

[b] For methods of calculation used in this table, see Appendix B, III.

TABLE 7-5. ESTIMATED LOSSES OF 3,3'-DICHLOROBENZIDINE, 3,3'-DIMETHYLBENZIDINE, AND 3,3'-DIMETHOXYBENZIDINE DURING PIGMENT PRODUCTION

Base	Optional tetrazonium filtration[a] (0.1-0.3%)	Losses in pigment formation[a,b] (0.5-1.0%)
3,3'-Dichlorobenzidine[c]		
1975	4-11	19-39
1976	5-16	26-54
1977	6-17	29-60
1978	7-22	37-76
3,3'-Dimethoxybenzidine[c]		
1975	0.2-0.7	1-2
1976	0.3-0.8	1-3
1977	0.3-0.8	1-2
1978	0.3-0.8	1-3
3,3'-Dimethylbenzidine[c]		
1975	0.02-0.05	0.1-0.2
1976	0.02-0.05	0.1-0.2
1977	0.02-0.05	~0.1
1978	-	-

[a] Estimated losses in terms of 1,000 lb.

[b] Losses include free base, unreacted tetrazonium compound, and soluble by-products resulting from the pigment production process.

[c] For methods of calculation used in this table, see Appendix B, III.

the free base or acid salt of 3,3'-dichlorobenzidine, 3,3'-dimethoxybenzidine, and 3,3'-dimethylbenzidine and the corresponding tetrazonium compounds. Estimated pigment losses resulting from subsequent transfer and handling procedures are presented in Table 7-6. Percentage loss ranges for each source of loss were discussed earlier in the pigment manufacture subsection. Once the pigment presscake is formed, the three processes delineated earlier can occur. The estimated losses resulting from shipment of the presscake are less than if the pigment is shipped as a dry toner or flushed color. Data for the percent distribution among the three processes were available only for the pigments derived from the dichlorobenzidine. Therefore, in Table 7-6, pigments resulting from either the dimethylbenzidine or dimethoxybenzidine were assumed to be the dry toner or flushed color (loss ranges are the same). Data from the ITC on the distribution of dichlorobenzidine-based pigments among the three processes are as follows (ITC, 1976a; 1977a; 1978a; 1979):

	1975 (%)	1976 (%)	1977 (%)	1978 (%)
Yellow 12				
Dry, full-strength toner	27.3	31.2	36.6	46.7
Flushed color	70.4	67.6	49.1	50.9
Presscake and dispersions	2.3	1.2	14.3	2.4
Yellow 14				
Dry, full-strength toner	(a)	(a)	(b)	59.3
Flushed color	(a)	(a)	(b)	4.4
Presscake and dispersions	(a)	(a)	(b)	36.3
All other DCB pigments				
Dry, full-strength toner	53.0	58.6	(c)	66.8
Flushed color	14.1	13.0	(c)	12.4
Presscake and dispersions	32.9	28.4	(c)	20.8

(a) Included with all other DCB pigments.
(b) Included with Yellow 12.
(c) Assumed 1976 percentages.

In 1977, Yellow 14 was removed from all the other DCB pigments category and combined with Yellow 12. The ITC distribution for these two pigments in 1977 was dry, full-strength toner (36.6%), flushed color (49.1%), and presscake and dispersions (14.3%). No data were provided for all other DCB pigments; the 1976 percentages were assumed for 1977. The percentages are applied to the appropriate production quantities presented in Table 7-3. After the quantity of each DCB pigment is calculated for the processing method (i.e. toner, flush color, and presscake), the percent loss ranges shown in Table 7-6 are used to estimate the losses for each method.

A quantity of dichlorobenzidine dihydrochloride normally is present in the presscake and is incorporated into a flushed color or dry toner. Industry sources state that the level of dichlorobenzidine dihydrochloride found in

TABLE 7-6. ESTIMATED PIGMENT LOSSES DUE TO TRANSFER AND HANDLING AT PRODUCTION FACILITIES, QUANTITY (1,000 lb)

Source of loss	% Loss range	1975			1976			1977			1978	
		DCB[a]	DMOB[b]	DMB[c]	DCB	DMOB	DMB	DCB	DMOB	DMB	DCB	DMOB
Dry toner - handling losses	1-3	36-112[d]	6-19	0.5-1	57-177	7-21	0.5-1	61-191	6-20	0.4-1	99-309	6-20
Flushed color - handling losses	1-3	48-148	ND[e]	ND	61-186	ND	ND	63-193	ND	ND	67-206	ND
Presscake transfer	0.5-1.0	7-14	ND	ND	8-17	ND	ND	13-26	ND	ND	11-22	ND
Pulverizer cleaning (optional)[f]	0.5-1.0	(18-37)	(3-6)	(0.2-0.5)	(28-58)	(3-7)	(0.2-0.5)	(30-62)	(3-7)	(0.2-0.4)	(49-101)	(3-7)
Blender cleaning (optional)[f]	0.5-1.0	(18-37)	(3-6)	(0.2-0.5)	(28-58)	(3-7)	(0.2-0.5)	(30-62)	(3-7)	(0.2-0.4)	(49-101)	(3-7)
Total Loss of Pigment (excludes optional sources)		91-274	6-19	0.5-1	126-380	7-21	0.5-1	137-410	6-20	0.4-1	177-537	6-20
Final Quality of Pigment (sold and for captive use)[g]		9,666-9,781	587-617	40-45	13,324-13,434	670-700	40-45	14,787-15,007	624-654	35-40	18,641-18,866	640-670

---

[a] Pigments based on 3,3'-dichlorobenzidine; for estimated quantities see Table 7-3.

[b] Pigments based on 3,3'-dimethoxybenzidine; for estimated quantities see Table 7-3.

[c] Pigments based on 3,3'-dimethylbenzidine; for estimated quantities see Table 7-3.

[d] For methods of calculation used in this table, see Appendix B, IV.

[e] ND = Not determined; all pigments derived from dimethoxybenzidine and dimethylbenzidine were assumed to be sold as dry toner.

[f] Data apply only to quantities sold as dry toner (see p. 7-17).

[g] See Table 7-3.

most pigments is approximately 20 ppm. These same sources indicated that imported quantities of pigments appeared to contain approximately the same level of dichlorobenzidine dihydrochloride as the U.S. material. Based on information derived from these sources, an estimate of the probable accuracy of the levels of dichlorobenzidine dihydrochloride in the finished pigment would be 20 ± 10 ppm. It is assumed that the levels are the same in the pigments derived from 3,3'-dimethylbenzidine and 3,3'-dimethoxybenzidine as they are for pigments based on 3,3'-dichlorobenzidine. Using a 20 ppm level and data from Table 7-6, the estimated quantities of 3,3'-dichlorobenzidine dihydrochloride present in the presscake pigments were 90 to 300 lb (1975), 135 to 400 lb (1976), 150 to 450 lb (1977), and 190 to 570 lb (1978). For dimethoxybenzidine, the estimated quantities present in the presscake pigments were 6 to 20 lb (1975), 7 to 20 lb (1976), 7 to 20 lb (1977), and 7 to 20 lb in 1978. For dimethylbenzidine, the estimated maximum quantities were approximately 1 lb for all 4 years. The above quantities include the estimated error factor of ± 50% for the 20 ppm level.

PIGMENT USAGE

The usage of the pigments within various product areas was derived from industry sources and a recent report (Powell et al., 1979). Data presented for the percentage consumption of a given pigment in each area are a synthesis of the information received and do not represent the specific opinion of any one source. The opinions were weighted to a certain extent depending upon the degree of involvement of the particular source in a specific area of use. The percentage utilization of each pigment in various applications is given in Table 7-7.

TABLE 7-7. CONSUMPTION OF PIGMENT BY USE AREA

	Percent					
Pigment	Printing ink	Plastics	Coatings	TPI[a]	Rubber	Other
Red 38	-	75	25	-	-	-
Red 41	-	99	1	-	-	-
Orange 13	45	45	5	-	5	-
Orange 15	-	-	-	-	-	100
Orange 16	30	30	6	20	-	14
Orange 34	-	-	-	100	-	-
Yellow 12	97	-	3	-	-	-
Yellow 13	70	8	7	15	-	-
Yellow 14	60	7	1	30	2	-
Yellow 17	50	25	25	-	-	-
Yellow 55	70	30	-	-	-	-
Yellow 83	35	25	10	30	-	-
Blue 25	-	-	4	96	-	-

[a] TPI = textile printing ink.

The percentage distribution for Yellow 17 is for 1978. Prior to that year, the distribution was printing ink, 40%; plastics, 30%; and coatings, 30%. Aside from the use of the yellow pigments in the printing ink industry, the percentage application in each area remained essentially the same from 1975 to 1978. In the printing ink industry, yellows have been extensively employed as a replacement for chromes. In addition, a considerable amount of interchanging between the various diarylide yellows has also occurred. It would be very difficult to chronicle the interactions between the various yellow pigments during the period 1975 to 1978. Therefore, the percentage distribution shown in Table 7-7 will be employed in the estimation of losses in Section 9, but it must be recognized that interactions among the yellow pigments have transpired.

SECTION 8

PLASTICS AND RUBBER INDUSTRY

This section discusses the use of pigments by the plastics and rubber industries. The pigments employed to color plastics and rubber and the types of resins colored are identified. Estimates of the quantities of pigments consumed by type of resin and total pigment loss (by compounding process) for each resin are estimated for 1975 through 1978.

INDUSTRY OVERVIEW - PLASTICS

Total plastics sales for the years 1975, 1976, 1977, and 1978 were 23,521 x 10^6, 29,168 x 10^6, 31,059 x 10^6, and 33,995 x 10^6 lb, respectively (Modern Plastics, 1976-1979).

Nine resins were identified that employed, in varying degrees, the pigments Reds 38 and 41, Oranges 13 and 16, and Yellows13, 14, 17, 55, and 83 (Modern Plastics Encyclopedia, 1978-1979). These resins are ABS, nylon, polyester, low density polyethylene (LDPE), high density polyethylene (HDPE), polypropylene, polystyrene, polyurethane, and polyvinyl chloride. There are two types of polyesters: thermoplastic and thermoset. In this report, the data have been limited only to the thermoset. These resins comprised ~76% of the total plastics production in 1975, ~77% in 1976, and ~80% in 1977 and 1978. Table 8-1 presents data for total production and production of colored resins for each of the nine resins during 1975 through 1978.

A brief discussion of each resin and the pigments used in the coloration of that resin is presented in the following paragraphs.

ABS

ABS (acrylonitrile, butadiene, and styrene) is a basic three monomer system that can be tailor-blended to meet a variety of specifications and as such can be used in a wide spectrum of applications. Red 38 and Yellow 13 are the most commonly used pigments while Yellows 14 and 17 and Orange 13 find minor usage.

ABS resins can be processed by all techniques common to thermoplastics although approximately 93% of the processing involves molding or extrusion (Modern Plastics Encyclopedia, 1978-1979). ABS is slightly hygroscopic, and drying for 2 to 4 hr at approximately 80°C is required prior to molding or extrusion.

TABLE 8-1. PRODUCTION OF SELECTED RESINS, 1975-1978

	Quantity (million pounds)							
	1975		1976		1977		1978	
Resin	Total	Colored	Total	Colored	Total	Colored	Total	Colored
Thermoplastics								
ABS	644	419	931	705	1,058	765	1,120	804
Nylon	144	(22)	209	(33)	249	(38)	271; 237a/	(40)
PVC	3,749	2,931	4,637	3,813	5,243	3,967	5,770	4,210
LDPE	4,736	2,041	5,788	2,698	6,502	2,903	7,025	3,092
HDPE	2,311	1,807	3,124	2,270	3,565	2,374	4,084	2,515
Polypropylene	1,899	1,280	2,597	1,838	2,703	1,871	2,957	1,977
Polystyrene	2,282	1,984	2,655	2,535	2,796	2,601	3,027	2,964
Thermosets								
Urethane	1,354	(68)	1,627	(80)	1,733	(87)	1,852	(93)
Polyester/alkyd	772	(193)	948	(240)	1,045	(261)	1,155	(289)
Total	17,890	10,740	22,520	14,210	24,890	14,870	27,260	15,980
% of total plastic production	76%		77%		80%		80%	

Source: Modern Plastics, September 1977-1978 and January 1977-1978; MRI estimates are shown in parentheses.

a/ Industry source.

Extruded sheet ABS can be thermoformed by heat and pressure/vacuum. The sheet may be embossed or have a laminate applied as the sheet passes through calendering/cooling rollers. Processing temperatures of 195 to 233°C are normally employed.

Nylons

Nylons are any long-chain synthetic polymeric amides with the amide group recurring as an integral part of the polymer chain. Yellows 14 and 17, and to a lesser extent Yellow 13, are the diarylide pigments used in nylons.

Nylon 6/6 and Nylon 6 are general purpose resins which are offered in a wide range of formulations and properties. Both resins can be processed by injection molding or extrusion. According to a major nylon manufacturer, industry data indicate that the combined consumption of Nylons 6/6 and 6 accounted for approximately 84% of total nylon consumption in 1978 (134×10^6 lb of Nylon 6/6 and 66×10^6 lb of Nylon 6).

Nylons 6/10 and 6/12 are specialty materials with low moisture absorption characteristics and are used in applications where stringent design characteristics are required. Injection molding and extrusion are the most prevalent processes by which products containing Nylons 6/10 and 6/12 are produced.

Nylons 11 and 12 are also considered specialty nylons. Like Nylons 6/10 and 6/12, they possess low moisture absorption characteristics. These nylons are mainly used in extrusion, fluidized bed, and electrostatic coating operations. According to an industry source, 1978 consumption of Nylons 6/10, 6/12, 11, and 12 was 7 to 8 million pounds.

All nylons are naturally hygroscopic (Modern Plastics Encyclopedia, 1978-1979). If supplied in moisture-proof packages, the nylon can be directly processed. Nylon resins supplied in open packages or regrind (waste resin processed by reuse) are dried in a vacuum or dehumidifying oven at about 80°C for 3 hr to decrease the moisture content to less than 0.3%.

The 1978 consumption statistics for the nylons varied somewhat according to the source. A trade publication (Modern Plastics, see Table 8-1) stated that 271 million pounds were consumed but an industry source estimated that 237 million pounds were sold domestically in resin form in 1978. The industry data will be used in this discussion.

Polyester/Alkyd

Alkyd molding compounds are thermoset materials produced by mechanically mixing polyester resins, cross-linking monomers, catalysts, mold release agents, mineral fillers, and fibrous reinforcements. These materials are supplied in three forms: a free-flowing granular form used where low impact strength is required; an extruded form supplied as preweighed logs or continuous rope used where medium impact strength is required; and bulk, where compression molding produces parts requiring high impact strength.

Polyester alkyds exhibit good dimensional stability and dielectric properties, which makes them especially useful in a wide range of electrical applications.

Granular and extruded forms of polyester can be compression, transfer, or injection molded. When compression or transfer molding the granular form, a preforming operation is normally required. Since the extruded material is not free-flowing and cannot readily be fed by a continuous process, specialized machinery is required to injection mold this resin. The bulk form is normally compression molded.

Of the pigments under consideration, only Orange 16 is employed in any extent with polyester/alkyds. Minor usage is found for Red 38, Orange 13, and all of the yellows.

Polyethylene

The complex reactions by which polyethylene is produced result in the availability of hundreds of different compounds with widely different properties. Polyethylene production represents > 30% of the total plastic resin market. LDPE is normally produced in autoclaves or tubular reactors with reaction pressures of up to 50,000 psi and temperatures up to 300°C. HDPE is produced by several low pressure polymerization processes; solution and slurry processes using Ziegler or Phillips-type catalysts are the two major methods. A gas-phase process is gaining increased importance; the process works by continuously feeding gaseous monomer and a catalyst to a fluidized bed reactor at reaction pressures of only 100 to 300 psi and temperatures of ≥ 100°C (Modern Plastics Encyclopedia, 1978-1979).

Polyethylene products can be fabricated by every processing method used for thermoplastics, but blow-molding, injection molding, and extrusion account for the bulk of production.

For LDPE, Orange 13 and Yellows 14 and 17 are the common pigments. There is minor usage for Reds 38 and 41, Orange 16, and Yellows 13, 55, and 83. In HDPE, Orange 13 and Yellow 17 are widely used, and Orange 16 and the remaining yellows find minor usage.

Polypropylene

Polypropylene is a thermoplastic consisting of an ordered arrangement of repeating propylene monomer units in a chain-like configuration. A stripping process at the end of the polymerization cycle is used to reduce an amorphous portion of the product (~ 10%) which, when present, has a negative effect on physical properties. Processing techniques widely used with polypropylene include extrusion and injection molding.

Yellow 17 is the only diarylide pigment with wide application in polypropylene. Oranges 13 and 16 along with Yellows 14, 55, and 83 find minor usage in this resin.

Polystyrene

General-purpose polystyrene is a transparent, rigid, glass-like homopolymer. When modified with rubber, an opaque and impact resistant resin is produced.

The predominant industrial processes used to produce polystyrene are mass (or bulk), solution, and suspension free radical polymerization. A combination of mass and suspension methods may be employed (Modern Plastics Encyclopedia, 1978-1979).

Polystyrene can be processed by all conventional thermoplastic fabrication techniques, but injection molding and sheet extrusion are probably the two most popular methods. Processes exhibiting significant growth include structural foam molding, injection- and extrusion-blow molding, profile extrusion, and coextrusion.

Only Orange 13 finds wide usage in polystyrene; Red 38 and all of the yellow pigments find minor usage.

Polyurethanes

Polyurethanes, also commonly called urethanes, are made by chemical reaction of an isocyanate and a polyol. Flexible foam, rigid foam, and elastomers comprise the three broad groups of urethanes.

Most flexible foam employs toluene diisocyanate (TDI); less commonly, polymethylenepolyphenyl isocyanate (PMPPI) and polyethers. Continuous lines, which produce slab flexible foam, are the most common manufacturing process. Flexible foams produced by this method are the low density and intermediate density foams. High resilience (HR) foams are produced by filling hot-cure foam with up to 50% clays, silica, and calcium carbonate.

Rigid foams include isocyanurates as well as urethane products. Applications are mainly for insulation products. In addition, the foams can be sprayed, poured in place, frothed, laminated, or foamed into buns which are cut into broadstock. Orange 13 and Yellow 14 are widely used in polyurethane; Red 38 and the remaining yellows (13, 17, 55, and 83) find minor usage in this resin.

Polyvinyl Chloride

Polyvinyl chloride (PVC) is a versatile, widely used polymer finding application in areas where requirements range from very soft and flexible to very rigid. Polyvinyl chloride is manufactured by four basic polymerization processes: suspension, solution, emulsion, and mass (or bulk).

Major additives used in compounding PVC are heat stabilizers, lubricants, processing aids, impact modifiers, plasticizers, fillers, and pigmentation systems.

PVC resins are available as pellets, powders, or in liquid dispersions. Powders or dry-blends are normally compounded through the use of ribbon blenders or high-intensity mixers. Optimum mixing is achieved by varying the time and temperature at which additives are introduced. The powder or dry-blend can be used directly or compounded into pellets. In the compounding step the powder or dry-blend is transformed into a melt by heat and mastication and then pelletized.

Liquid forms include plastisols and organosols. Dispersions of homopolymers and vinyl acetate copolymers of vinyl chloride in plasticizers are termed plastisols; organosols are plastisols containing a volatile diluent necessary to lower the paste viscosity without increasing the plasticizer level. Pigments are added to a plastisol in a predispersed pigment--plasticizer paste prepared on a three roll paint mill.

The majority of the PVC is processed by extrusion, injection molding, blow molding, and calendering. Powder coating and liquid processing are less commonly used processes.

Numerous diarylide pigments find wide usage in both flexible and rigid PVC. Yellows 17, 55, and 83, and Oranges 13 and 16 are widely used in both types of PVC. In addition, Red 38 and Yellow 13 are widely used in flexible vinyl but find only minor usage in the rigid vinyl. Red 41 and Yellow 14 find only minor usage in either form of PVC.

PIGMENT CONSUMPTION - PLASTICS

Nine of the diarylide pigments under study are used in the plastics industry. These pigments were delineated in the previous subsection; estimated consumption of each pigment for 1975 through 1978 is presented in Table 8-2.

The degree of application for each of these pigments with respect to specific resins was discussed in the previous subsection.

Colorant Addition

Mixing and compounding are the principal stages in plastics production during which additives, such as pigments, are incorporated into the resin. Some resins such as polyethylene and polypropylene use only small amounts of additives and, therefore, have no separate compounding stage. The additives are usually incorporated into the resin during an extrusion/compounding operation subsequent to the reaction process (Modern Plastics Encyclopedia, 1978-1979). Typical machines for this operation are continuous or batch internal mixers and single or twin-screw extruders. Other resins are compounded during a separate operation.

There are a variety of compounding machines including internal mixers, Banbury-type mixers, screw extruder (single or twin-screw), and various combinations of mixers and extruders.

TABLE 8-2. ESTIMATED CONSUMPTION OF PIGMENTS IN THE PLASTICS INDUSTRY

Pigment	Quantity (1,000 lb)[a/] 1975	1976	1977	1978
Red 38	(143-146)	154	154	(158-161)
Red 41	(40-60)	(40-60)	(40-60)	(40-60)
Orange 13	99	121	108	108
Orange 16	113	143	132	140
Yellow 13	13	32	40	42
Yellow 14	130	210	227	219
Yellow 17	125	230	301	343
Yellow 55	(15-18)	(15-18)	(27-33)	(42-48)
Yellow 83	(158-183)	(216-240)	(230-280)	(277-327)
Total	842-893	1,161-1,208	1,249-1,325	1,369-1,448

[a/] Quantities of 100% pigment derived from Tables 7-3 and 7-7. Values in parentheses are based on MRI estimates; all others are based on ITC data.

Diarylide pigments may be added to the resin in basically two forms: color concentrates or dry pigment. The dry pigment is added directly to a resin during the additive blending process. In a color concentrate, the pigment is predispersed in a medium such as the resin itself. Typically, 35 to 50% of the color concentrate is pigment. The ratio of the weight of the final colored resin to the weight of the concentrate is called the let-down ratio. This ratio usually ranges from 20:1 to 100:1, which means the concentration of pigment in the final resin ranges from 0.35 to 2.5% (Modern Plastics Encyclopedia, 1978-1979). Concentrates are usually supplied in pellet form but may also be supplied in flake form.

Pigment Usage

Contacts with industry representatives (pigment manufacturers and plastic formulators) and literature searches failed to provide the data necessary to complete a breakdown of specific pigment consumption in individual resins. In the absence of necessary data, several assumptions were made in order to derive estimations for specific pigment consumption in each of the nine resins.

One assumption is that approximately 90% of the total quantity of pigment was consumed in those resins for which the pigment found wide usage and 10% was in those resins for which the pigment had only limited usage. As an example, Yellow 14 is widely used in the following resins: nylon, LDPE, and polyurethane. It finds limited usage in ABS, polyester/alkyds, HDPE, polystyrene, polypropylene, and PVC. Thus, 90% of the total quantity of Yellow 14 consumed in plastics (approximately 219,000 lb in 1978) is used to color nylon, LDPE, and polyurethane; and 10% is used in ABS, polyester, HDPE, polystyrene, polypropylene, and PVC. The quantity of each colored resin produced annually was presented in Table 8-1. From these data, the quantity of each pigment utilized in the individual resins was prorated on the basis of either wide or limited usage and the total quantity of colored resin manufactured for each year. These data are presented in Tables 8-3 to 8-6.

The data in these tables assume no bias towards a specific resin. To use the Yellow 14 example, it is assumed that 90% of the total quantity of pigment is prorated on a weight basis between nylon, LDPE, and polyurethane according to the total quantity produced of each of the three resins. The same assumption is made for the area comprising 10% of the total consumption.

ESTIMATED LOSSES - PLASTICS

The majority of pigment losses from plastics is associated with the ultimate disposal of the consumer product. Few data were obtained from the plastics industry regarding losses of colorants in the resin compounding stage (i.e., formation of the colored resin). Based on other processing information, it is estimated that a 1 to 2% pigment loss occurs due to handling and transfer of powdered colorants or concentrates during the compounding of resins.

Estimates of pigment loss during processing were combined with data for the total quantity of pigment consumed by specific resins (Tables 8-3 to 8-6). The estimated losses (1-2%) of diarylide pigment due to handling and transfer of powdered colorants or concentrates from each resin for 1975 through 1978 are presented in Table 8-7.

Information was obtained from the plastic industry trade association for estimated resin losses during processing by plastics fabricators. Resin losses represent an additional source of pigment loss although the pigment has been incorporated into the resin and is not lost as the pure colorant. These losses range from 5 to 15% for thermoplastics and from 10 to 30% for thermosets. Of the resins listed in Table 8-1, all are thermoplastics except for polyester/alkyd and urethane. Fabrication waste reuse for thermoplastic production varies from company to company and from operation to operation. Unless the scrap thermoplastic is captively reprocessed or discarded because of contamination or too small a volume, the waste plastic from primary production and fabrication is acquired by scrap dealers or reprocessors. Reprocessing of thermoplastics may entail regrinding, washing, or reblending the scrap material. The reprocessed material is either sold or returned to the client in the reground form or converted to colored or black pellets. For thermoset wastes, those materials, which can be remelted, are reused. Those wastes, which cannot be remelted, have traditionally gone to disposal (SPI, 1979).

TABLE 8-3. ESTIMATED AMOUNT OF PIGMENTS CONSUMED BY RESIN (1975)
(Quantity in 1,000 lb)a/

									Vinyl			
Pigments	ABS	Nylon	Polyester/ alkyd	LDPE	HDPE	PP	Polystyrene	Urethane	Flexible	Rigid	Combined	Total
Red 38	31-31.7	-	0.5	4.9-5.1	-	-	4.8-4.9	0.2	97.7-99.7	3.9-4.0		143-146
Red 41	-	-	-	16.4-24.6	-	-	-	-			23.6-35.4	40-60
Yellow 13	3.6	-	0.05	0.6	0.5	-	0.6	0.02	13.7	-		19
Yellow 14	0.6	1.2	0.3	112.1	2.8	1.9	2.9	3.7			4.4	130
Yellow 17	2.1	0.3	0.9	28.3	25.3	17.9	9.2	0.3			40.8	125
Yellow 55	-	-	0.05	0.4-0.5	0.4	0.3	0.4-0.5	0.01			13.5-16.2	15-18
Yellow 83	-	-	0.4-0.5	4.4-5.0	3.9-4.5	2.7-3.1	4.2-4.9	0.1			142.3-164.9	158-183
Orange 13	0.2	-	1.1	20.2	18.7	7	20.6	0.6			30.5	99
Orange 16	-	-	6.3	4.5	4	2.8	-	-			95.4	113
Total	37.5-38.2	1.5	9.6-9.7	191.8-200.9	55.5-56.1	32.6-33.0	42.7-43.6	4.9	111.4-113.4	3.9-4.0	350.5-387.6	842-893

a/ Quantities in terms of 100% pigment.

Source: Estimates based on Modern Plastics, September issues 1976-1978 and January issues 1977-1979; and Modern Plastics Encyclopedia, 1978-1979. Data from Tables 4-3 and 4-6.

TABLE 8-4. ESTIMATED AMOUNT OF PIGMENT CONSUMED BY RESIN (1976)
(Quantity in 1,000 lb)[a]

Pigment	ABS	Nylon	Polyester/ alkyd	LDPE	HDPE	PP	Polystyrene	Urethane	Vinyl			Total
									Flexible	Rigid	Combined	
Red 38	40.1	-	0.5	5.5	-	-	5.6	0.2	97.5	4.6		154
Red 41	-	-	-	16.6-24.8	-	-	-	-			23.4-35.2	40-60
Yellow 13	7.3	0.01	0.1	1.1	0.9	-	1.0	0.03	21.6	-		32
Yellow 14	1.3	2.2	0.4	181.4	4.2	3.5	4.7	5.4			7.0	210
Yellow 17	4.5	0.6	1.5	52.6	44.2	16	16.1	0.6			74.1	230
Yellow 55	-	-	0.05	0.5-0.6	0.4-0.5	0.3-0.4	0.2	0.01			13.6-16.3	15-18
Yellow 83	-	-	0.7	6.8-7.6	5.7-6.3	4.6-5.2	2.6-2.9	0.2			195.5-217.2	216-240
Orange 13	3	-	1	25.8	21.7	8	24.2	0.8			36.4	121
Orange 16	-	-	7.5	5.6	4.8	3.9	-	-			121.1	143
Total	56.2	2.8	11.8	295.9-305	81.9-82.6	56.3-57	54.4-54.7	7.2	119.1	4.6	471.1-507.3	1,161-1,208

[a] Quantities in terms of 100% pigment.

Source: Estimates based on Modern Plastics, September issues 1976-1978 and January issues 1977-1979; and Modern Plastics Encyclopedia, 1978-1979.

TABLE 8-5. ESTIMATED AMOUNT OF PIGMENTS CONSUMED BY RESIN (1977)
(Quantity in 1,000 lb)[a]

Pigment	ABS	Nylon	Polyester/ alkyd	LDPE	HDPE	PP	Polystyrene (combined)	Urethane	Vinyls Flexible	Vinyls Rigid	Vinyls Combined	Total
Red 38	41.6	-	0.5	5.6	-	-	5.0	0.2	97	4.2		154
Red 41	-	-	-	17-25.2	-	-	-	-			23-34.8	40-60
Yellow 13	7.2	0.01	0.1	1.1	0.9	-	0.9	0.03	20	-		30
Yellow 14	1.5	2.6	0.5	195.7	4.5	3.6	5	5.9			7.7	227
Yellow 17	6	1	2.2	70.5	57.6	65.5	21.1	0.5			96.5	301
Yellow 55	-	-	0.1	0.9-1.1	0.07-0.9	0.6-0.8	0.4-0.5	0.03			24.3-29.7	27-33
Yellow 83	-	-	0.7-0.8	7.8-9.5	6.4-7.8	5.0-6.2	2.8-3.4	0.2-0.3			207-252	230-280
Orange 13	2.8	-	0.9	23.5	19.1	7	22	0.7			32.1	108
Orange 16	-	-	7.3	5.4	4.4	3.5	-	-			111.4	132
Total	59.1	3.6	12.3-12.4	327.5-337.6	93.6-95.2	65.2-66.6	57.2-58	7.7-7.8	117	4.2	502-564.2	1,249-1,325

[a] Quantities in terms of 100% pigment.

Source: Estimates based on Modern Plastics, September issues 1976-1978 and January issues 1977-1979; and Modern Plastics Encyclopedia, 1978-1979.

TABLE 8-6. ESTIMATED AMOUNT OF PIGMENTS CONSUMED BY RESIN (1978)
(Quantity in 1,000 lb)[a/]

Pigments	ABS	Nylon	Polyester/ alkyd	LDPE	HDPE	PP	Polystyrene (combined)	Urethane	Vinyls			Total
									Flexible	Rigid	Combined	
Red 38	42.4-43.2	-	0.5	5.6-5.7	-	-	5.3-5.5	0.2	99.8-101.7	4.2-4.3		158-161
Red 41	-	-	-	16.4-25.0	-	-	-	-			23.2-35.4	40-60
Yellow 13	10.4	-	0.01	0.1	1.5	-	1.4	0.04	28.6	-		42
Yellow 14	1.2	2.1	0.5	190.0	4.3	3.4	5.2	5.0			7.2	219
Yellow 17	6.6	0.5	2.3	80.5	66.2	51.8	24.7	0.8			109.6	343
Yellow 55	-	-	0.1	1.4-1.6	1.1-1.3	0.9-1.1	0.6	0.05			37.8-43.2	42-48
Yellow 83	-	-	0.8-1.0	9.3-11.0	7.7-9.0	6.0-7.1	3.6-4.3	0.3			249.3-296.4	277-327
Orange 13	2.9	-	1.0	23.3	19.0	7.0	22.4	0.7			31.8	108
Orange 16	-	-	8.0	5.7	4.7	3.7	-	-			117.9	140
Total	63.5-64.3	2.6	13.2-13.4	332.3-342.5	104.5-106.0	72.8-74.1	63.2-64.1	7.1	128.4-130.3	4.2-4.3	576.8-639.5	1,369-1,448

a/ Quantities in terms of 100% pigment.

Source: Estimates based on Modern Plastics, September Issues 1976-1978 and January Issues 1977-1979; and Modern Plastics Encyclopedia, 1978-1979.

TABLE 8-7. ESTIMATED PIGMENT LOSS IN RESIN COMPOUNDING STAGE

	Quantity (1,000 lb)			
	1975	1976	1977	1978
Total pigment used[a]	842-893	1,161-1,208	1,249-1,325	1,369-1,448
Resin - thermoplastic				
ABS	0.4-0.8	0.6-1.1	0.6-1.2	0.6-1.3
Nylon	0.02-0.03	0.03-0.06	0.04-0.07	0.03-0.05
LDPE	1.9-4.0	3.0-6.1	3.3-6.8	3.3-6.9
HDPE	0.6-1.1	0.8-1.7	0.9-1.9	1.0-2.1
Polypropylene	0.3-0.7	0.6-1.1	0.7-1.3	0.7-1.5
Polystyrene	0.4-0.9	0.5-1.1	0.6-1.2	0.6-1.3
Polyvinyl chloride	4.7-10.1	5.9-12.6	6.2-13.7	7.1-15.5
Total loss	8.3-17.6	11.4-23.8	12.3-26.2	13.3-28.7
Total in resin	810-870	1,118-1,178	1,203-1,293	1,320-1,414
Resin - thermoset				
Polyester/alkyd	0.1-0.2	0.1-0.2	0.1-0.2	0.1-0.3
Urethane	0.05-0.1	0.07-0.1	0.08-0.2	0.07-0.1
Total loss[b]	0.15-0.3	0.17-0.3	0.18-0.4	0.17-0.4
Total in resin	14.2-14.5	18.7-18.8	19.6-20.0	19.9-20.3

[a] See Tables 8-3 to 8-6.

[b] Percentage losses are as follows: 1975 (1.0-2.1%); 1976 (0.9-1.6%); 1977 (0.9-2.0%); and 1978 (0.8-2.0%).

Estimates of the total quantity of pigment in resin developed in Table 8-7 were combined with the percentage resin losses stated by SPI to provide a basis for the estimated pigment losses as a result of resin losses. These data are shown in Table 8-8.

TABLE 8-8. ESTIMATED PIGMENT LOSSES VIA RESIN PROCESSING

	Quantity (1,000 lb)			
	1975	1976	1977	1978
Total pigment in resin[a]				
Thermoplastic	810-870	1,118-1,178	1,203-1,293	1,320-1,414
Thermoset	14.2-14.5	18.7-18.8	19.6-20.0	19.9-20.3
Estimated pigment losses				
Thermoplastic (5-15%)	41-131	56-177	60-194	66-212
Thermoset (10-30%)	1-4	2-6	2-6	2-6
Total loss	42-135	58-183	62-200	68-218
Total quantity of pigment in finished product	689-843	954-1,139	1,023-1,251	1,122-1,366

[a] See Table 8-7.

INDUSTRY OVERVIEW - RUBBER INDUSTRY

Although rubber related industries can be divided into natural and synthetic rubber users, it is more advantageous for the purposes of this discussion to classify the industry according to the Standard Industrial Classification (SIC) codes. These are presented in Table 8-9.

The pigments under consideration in this report are probably not employed by industries in at least two of the five SIC codes listed. Tire and inner tube manufacturing (SIC 3011) uses small amounts of white pigment mainly titanium oxide, for the white walls on automobile and truck tires, but the remainder of the rubber is black as a result of the carbon black added to improve some of the physical properties of the finished rubber. Tire manufacturers do not use colored (nonblack) organic pigments.

Processes involved in reclaiming rubber (SIC 3031) could lead to degradation of the colorants and process wastes which may be different from the rest of the rubber industry; however, most of the scrap rubber used in this industry results from discarded tires and inner tubes which do not contain any of the pigments of interest. Therefore, SIC Codes 3011 and 3031 were excluded from any further consideration in this study.

TABLE 8-9. STANDARD INDUSTRIAL CLASSIFICATION (SIC) CODES FOR RUBBER AND MISCELLANEOUS PLASTIC PRODUCTS

SIC Code	Industry	Description of products
3011	Tires and inner tubes	Pneumatic casings, inner tubes, and solid and cushion tires for all vehicles, and camelback, tire repair and retreading materials.
3021	Rubber and plastics footwear	All rubber and plastics footwear, waterproof fabric upper footwear, and rubber or plastic soles.
3031	Reclaimed rubber	Devulcanized, depolymerized or regenerated replasticized products from scrap rubber tires, tubes and miscellaneous waste rubber articles.
3041	Rubber and plastics hose and belting	Industrial hose and belts and garden hoses.
3069	Fabricated rubber products, not elsewhere classified	Industrial and mechanical rubber goods, rubber fabrics, and miscellaneous rubber goods.

Source: Statistical Policy Division, 1972

The remaining industries, rubber and plastics footwear (SIC 3021), rubber and plastic hoses and belts (SIC 3041), and fabricated rubber products not elsewhere classified (SIC 3069) are the potential areas for the use of diarylide pigments.

Other considerations for the use of these pigments result from their higher cost in comparison to the inorganic pigments and the general lack of lightfastness displayed by some of the diarylide pigments. The primary use of the diarylide pigments in the rubber industry probably lies in housewares (e.g., mats for sinks and tubs) and toys, automobile accessories, and other household, automotive, or recreational products.

Data for 1978 show that 64.4% of all new rubber was used by the tire segment; no data were available on the amounts of rubber colored by pigments other than black or white (Rubber World, 1979). One estimate is that less than 10% of the rubber used is colored (Bleaskiewcz, 1979). If this estimate is correct, the total quantity of colored rubber would be approximately 700 million pounds. No data were obtained on the percent of rubber colored with organic pigments or with diarylide pigments.

RUBBER PRODUCTION PROCESS

The rubber industry is divided into two segments, natural and synthetic rubber. The rubber production process basically involves obtaining an elastomer by polymerization of compounds or extraction from rubber plants, mixing the elastomer with other chemicals, forming this mixture into a desired shape, and curing or vulcanizing to produce a crosslinked thermoset structure. It is the crosslinked structure which produces the rubber-like qualities.

Natural rubber is extracted from trees as field latex, a dispersion of small rubber particles in water, which is then processed into either a latex form or dry rubber.

The synthetic elastomers are produced by polymerizing various monomers depending upon the specific properties desired in the final product. The polymerization may take place in an emulsion or in a solvent which leads to only slightly different steps in removal of the water or solvent. The synthetic rubber may be utilized as a latex, but most often it is dried and used as dry rubber. The production of the various types of rubber for 1975 through 1978 is shown in Table 8-10.

Once the elastomer is produced, the next step is compounding, during which various additives are mixed with the elastomer to impart specific properties to the finished rubber. Carbon black and other inorganic fillers and pigments are sometimes added to the rubber; other chemicals added during compounding include the vulcanizing agents necessary to produce the cross linkage characteristics of rubbers, accelerator for vulcanization, and antioxidants and antiozonants.

The next step in rubber production is the shaping or molding of the rubber. The mixture may be molded by three methods: compression, transfer,

TABLE 8-10. U.S. RUBBER PRODUCTION BY TYPE, 1975-1978

Type of rubber	Quantity ($\times 10^6$ lb) 1975[a]	1976[a]	1977[a]	1978[a]
SBR	2,606	2,979	3,252	2,994
Butyl	183	276	329	340
N-type	119	165	161	161
Polybutadiene	655	781	796	856
Polyisoprene	135	163	137	[b]
EPDM	185	302	348	386
Silicone	31	37	53	78
Styrene-butadiene-vinylpyridine	29	31	33	43
Urethane type	57	82	93	112
Other	637	650	701	902
Total	4,637	5,466	5,905	5,872

[a] 1975-1978 production figures were obtained from ITC, 1976a; ITC, 1977a; ITC 1978a; and ITC, 1979.

[b] Included in Other in 1978.

or injection. Compression molding is the most common and the simplest. Transfer molding transfers the rubber from a larger container into the mold; the method usually produces more waste but also gives better dimensional control. Injection molding utilizes a screw device which injects the rubber into a mold. Rubber can also be treated by other processing methods, such as calendering. After molding, the rubber is vulcanized to cross link the molecules.

PIGMENT CONSUMPTION - RUBBER

Industry sources estimate that only two of the pigments being considered in this study are used in the rubber industry. Approximately 2% of the total consumption of Yellow 14 and about 5% of Orange 13 are employed in the manufacture of rubber products. Table 8-11 presents estimated consumption of these two pigments from 1975 through 1978. Small quantities of other diarylide pigments may be used in the rubber industry; however, Orange 13 and Yellow 14 were the only two pigments specifically identified in this study and for which consumption data could be reliably estimated.

TABLE 8-11. CONSUMPTION OF PIGMENTS - RUBBER INDUSTRY

	Quantity (1,000 lb)[a]			
Pigment	1975	1976	1977	1978
Orange 13	11	13	12	12
Yellow 14	37	60	65	63

[a] Quantities of 100% pigment derived from Tables 7-3 and 7-7.

ESTIMATED LOSSES - RUBBER

Although other losses occur during the production of elastomers, the loss of pigment begins with the compounding of the rubber. One of the primary considerations in the determination of losses during compounding is whether the pigment is added in a dry form or as a masterbatch. A masterbatch consists of a quantity of pigment dispersed in an equal amount of dry rubber, resin, or plasticizer. Although an estimated 45% of the pigment used by the rubber industry is purchased as dry pigment (Greer, 1979), the pigment will almost always be mixed by the rubber producer to form a masterbatch (Bleaskiewcz, 1979). Reasons for this include easier measurement of an exact quantity of pigment, less pigment waste, and less dust to contaminate the compounding machines.

It is estimated that little pigment loss (~ 0.1-0.3%) would occur as dust during the actual compounding stage. During production of a masterbatch, pigment losses occur as dust from handling and transfer of the pigment. Because specific information could not be identified concerning the magnitude of these losses, an estimated loss of 0.1 to 0.5% has been assumed based on similar procedures in the coatings industry (see Section 10). The dust would likely be collected as floor sweepings or in collection containers of air filter devices. These solid wastes are disposed by landfilling (Snell, 1978).

The cleaning wastes in compounding, shaping, and molding are assumed to be small. The compounding equipment may be cleaned with a solvent or by the use of excess dry rubber called clean-out rubber. The clean-out rubber is used repeatedly until it becomes too contaminated for further usage. At this point the contaminated clean-out rubber is landfilled with the rest of the rubber waste.

Excess rubber is produced from shaping, molding, and finishing. Losses due to uncured scraps from the shaping and molding steps are estimated to be 4.2% for the rubber footwear industry and 2.2% for the rubber and plastics hose and belting industry (Snell, 1978). Although a composite figure could be calculated for the loss of uncured rubber stock, a range of 2.2 to 4.2% loss was utilized due to the very small total consumption of pigments in this industry. The waste from uncured rubber stock is usually landfilled.

Uncured scraps of rubber are also created in the finishing steps. In general, these scraps result from flash trimmings (excess rubber in molds), miscellaneous scraps, and rejects. Estimates of these wastes range from 1 or 2% to approximately 30% (based on Snell, 1978). The general practice is to landfill this waste.

An estimate of the total quantity of pigment loss in the rubber industry is presented in Table 8-12 for 1975 through 1978.

TABLE 8-12. ESTIMATED PIGMENT LOSS IN THE RUBBER INDUSTRY

	Quantity (1,000 lb)[a]			
	1975	1976	1977	1978
Total Pigment in Rubber[b]	48	73	77	75
Estimated Pigment Losses				
Compounding (0.1-0.3%)	0.05-0.1	0.07-0.2	0.08-0.2	0.08-0.2
Masterbatch (0.1-0.5%)	0.05-0.2	0.07-0.4	0.08-0.4	0.08-0.4
Shaping, Molding, and Finishing (2.2-4.2%)	1.1-2.0	1.6-3.1	1.7-3.2	1.7-3.2
Total Loss	1.2-2.3	1.7-3.7	1.9-3.8	1.9-3.8
Total Quantity of Pigment in Rubber	45.7-46.8	69.3-71.3	73.2-75.1	71.2-73.1

a/ Quantities in terms of 100% pigment.

b/ See Table 8-11.

SECTION 9

PRINTING INKS

Printing inks, especially the process inks used in color printing, represent the major industrial use of the pigments based on 3,3'-dichlorobenzidine (DCB) or 3,3'-dimethoxybenzidine (DMOB). Approximately 11.5 million pounds, or 76% of all the diarylide pigments produced in 1977, were consumed in the form of printing ink. A detailed examination of the patterns of pigment usage and losses to the environment associated with the production and use of printing inks will serve to place in perspective the distribution of diarylide compounds and routes of entry into various media.

INDUSTRY CHARACTERISTICS

The ink industry (SIC 2893) comprises an estimated 460 to 500 manufacturing establishments operated by approximately 200 companies. In addition, there are estimated to be 100 captive ink manufacturing sites within printing companies who manufacture inks for their own use. Current data are not available on the ink production activity within SIC 27, Printing and Publishing. The 1972 Census of Manufactures placed the number of ink manufacturing plants at 407 establishments having a total of 9,600 production employees. The 1977 Census reported 452 establishments, of which 158 had more than 20 employees.

The survey conducted in 1978 (Burns and Roe, 1979a) obtained responses from 460 ink manufacturing sites that reported production and employment on the basis of 1976 operations. The data obtained through this survey are considered by MRI adequate to reflect the current characteristics of the industry.

There are a large number of small ink manufacturing plants. Forty-two percent of these plants have fewer than 10 employees; and 71%, fewer than 20 employees. However, these smaller plants accounted for only 25.5% of ink shipments in 1972. The 130 plants (28.3%) having more than 20 employees shipped 75% of the total ink sold.

A moderate degree of concentration is found in ink manufacture. Thirteen companies operate 51% of all plants, and six larger companies (Borden, Inmont, Sun Chemical, Flint Ink, Sinclair and Valentine, and Kohl and Madden) account for 37% of all ink manufacturing plants. Ink manufacturing establishments are generally located in metropolitan areas where large volumes of printing are performed. Slightly over 50% of all large ink plants (> 30 employees) are located in the states of New Jersey, Illinois, Ohio, and

California. Sixty-four percent of all plants are branch plants of a multiple plant company (Burns and Roe, 1979a).

Total ink shipments for 1977 were valued at $960.2 million, up 93% over 1972 shipments. The volume of ink produced in each plant ranges from less than 200,000 lb/year to over 3 million pounds annually (Table 9-1).

TABLE 9-1. 1976 PRODUCTION VOLUME IN POUNDS

Volume pounds	Plants	Percent of plants
Under 200,000	121	28.8
200,000 to 500,000	76	18.1
500,000 to 1 million	79	18.8
1 million to 3 million	75	17.9
Over 3 million	69	16.4

Source: Burns and Roe, 1979a.

Due to the increasing demand for commercial printing, the physical output of the printing ink industry has been growing substantially. Present data are not adequate to characterize the rate of growth for different types and classes of printing inks. The distribution of shipments of ink in 1977, by type of ink, is given in Table 9-2.

TABLE 9-2. 1977 INK SHIPMENTS BY TYPE OF INK

Ink type	Value million dollars	Percent of shipments
Letterpress	119.6	12.5
Lithographic	281.2	29.3
Gravure	194.5	20.3
Flexographic	194.7	20.3
Other types	61.3	6.4
Not classified	108.9	11.3
Total	960.2	100.0

Source: Census of Manufactures, 1977.

There have been, and will continue to be, major shifts among the types of printing processes employed and the kinds of ink used. Gravure and flexographic ink output has been growing rapidly in recent years. Lithography has grown steadily and currently represents 56% of all commercial printing. Letterpress (except for flexography) has continued its downward slide, even in long run daily newspapers. According to one industry source, the anticipated changes among printing processes are shown in Table 9-3. Gravure, lithography and flexography will account for 89% of press operations by 1990, while traditional letterpress printing will decline by over two-thirds.

TABLE 9-3. DISTRIBUTION BY PRINTING PROCESS

Process	1977	1980	1990
Letterpress	32%	25%	10%
Flexography	11%	12%	15%
Lithography	38%	40%	40%
Gravure	14%	17%	25%
Screen printing and other processes	5%	6%	10%

Source: Bruno, 1978.

INK PRODUCTION BY TYPES

The wide variety of printing inks employed ranges from newspaper inks to specialized electrostatic jet printing inks. However, most of the inks produced for printing can be classified into two viscosity ranges and four main types of inks:

Paste Inks	Fluid Inks
Letterpress	Flexographic
Lithographic	Gravure

Letterpress inks are viscous, tacky, resinous pastes, typically made using vehicles that are oil and varnish based, and solvent thinned. Drying occurs by the oxidation of the varnish type vehicle.

Lithographic (sometimes called offset inks) are viscous inks with an oleoresinous, varnish-based vehicle, generally thinned with organic solvents. Because lithographic inks are applied in thinner films, the pigment content is higher than in letterpress inks, and pigments of high tinting power and good color saturation are employed. Lithographic inks are designed to be water resistant and to run in the presence of water since a water film is used to create the nonimage areas of the printing plate.

Flexographic inks (a subcategory of letterpress printing in which raised rubber type carries the ink to the surface) are liquid inks which dry by evaporation of the carrier and by absorption into the substrate. Both waterborne and solvent vehicles are used in flexography; water inks are used on absorbent paper, and solvent inks are used on packaging films and nonabsorbent surfaces.

Gravure inks are liquid inks which dry by evaporation of the solvent carrier. Three subtypes of gravure inks are recognized. "Publication" inks used for catalogs and magazines are designed to have superior color characteristics and sharp printing properties. "Supplement" inks used for advertising supplements to newspapers employ less costly pigments and are designed to perform high speed printing on more absorbent papers. Both publication and supplement inks have fairly well standardized properties. "Packaging" inks, the third subtype, are much more varied and are formulated individually for printing on films, foils, coated papers, and the variety of materials used in the packaging field (Welch, 1979).

Table 9-2 gave the relative percentage of each of the main types of ink used in 1977 in terms of value of shipments. Letterpress inks are less costly than the other three types of ink. Although 32% of all printing is performed with letterpress inks, the value of the ink represents less than 13% of total dollar volume of all printing inks. Lithographic inks represent 30% of the total value, and because ink "mileage" is greater with lithographic inks (thin ink films are laid down), nearly 40% of all printing is run on lithographic presses.

The Gravure Technical Association survey team reported (Maida, 1978) that a conservative estimate of gravure ink consumption in 1976 could be broken down as follows:

Subtype	Million pounds	Value (million dollars)
Publication inks	180	90
Packaging and specialty	150	120
Total	330	210

Most gravure printing is in color; the distribution of ink colors are: black, 32.0%; magenta (red), 23.5%; cyan (blue), 25.9%; and yellow, 48.9%. A large proportion of the diarylide yellow pigments are used in the production of gravure inks.

Other types of ink such as screen process printing inks, metallic inks, magnetic inks, virkotype and electrostatic jet printing inks are very diverse and specialized. Ink experts generally agree that specialty inks do not consume significant quantities of the diarylide organic pigments. Textile printing inks, although sometimes considered as part of the printing ink field, were discussed in the textile dyeing and printing section.

MANUFACTURE OF PRINTING INKS

Virtually all printing inks are produced in batches--sometimes large batches exceeding 10,000 lb; more often in batches ranging from 100 to 500 lb at a time.

The essential steps in the production of printing inks generally include:

1. Weighing the ingredient for a batch into a mixing tub.

2. Dispersing (grinding) the pigments into the vehicle.

3. Adjusting the properties of the ink to final specifications (e.g., adding thinners, additives, tinting colors, and blending to uniformity).

4. Packaging for delivery to the user.

5. (Sometimes) cleanup of equipment.

It is convenient to discuss the handling of diarylide pigments, the range of losses of ink and pigment during production, and the levels of pigment discharged to environmental media in terms of these basic steps in production.

Pigment Usage

For purposes of detailing the fate and distribution of pigments based on DCB or DMOB, only the organic pigments used and the types of vehicles employed--paste or liquid, solvent or water-based--will be considered.

The diarylide pigment yellows and oranges are used extensively in the manufacture of printing inks. For many years the diarylide yellow pigments have dominated the market for organic yellow toners. As early as 1969, diarylides accounted for 84% of total U.S. organic yellow pigments (Patton, 1973). By 1978, total diarylide production in the United States had risen to an estimated maximum of 19.5 million pounds, with the distribution shown in Table 4-6. Yellow 12 is still the dominant pigment at 11.9 million pounds (61.0% of all diarylide pigments). Yellow 14, with an estimated production of 3.1 million pounds, accounts for 15.9% of all diarylides. Since 1976, Orange 13 has generally declined in usage, and Yellow 17 has almost doubled in production volume. The only significant addition since 1969 has been Yellow 83, which was not reported separately prior to 1976, and had an estimated production volume of 1.2 million pounds in 1978.

Total consumption of diarylide pigments in printing inks amounted to an estimated maximum of 15.2 million pounds in 1978. This usage accounted for 77.9% of all the diarylide pigments under consideration in this study. Table 9-4 presents the best available industry data regarding printing ink

TABLE 9-4. ESTIMATED DIARYLIDE PIGMENT CONSUMPTION IN PRINTING INKS

Pigment	Percent in ink[a]	Quantity[b] (1,000 lb)			
		1975	1976	1977	1978
Orange 13	45	99	121	108	108
Orange 16	30	113	143	132	140
Yellow 12	97	5,907	7,629	8,438	11,506
Yellow 13	70	170	280	260	364
Yellow 14	60	1,111	1,800	1,949	1,881
Yellow 17	40 (1975-1977)	166	307	401	
	50 (1978)				685
Yellow 55	70	(35-42)	(35-42)	(63-77)	(98-112)
Yellow 83	35	(222-257)	(300-335)	(322-392)	(387-457)
Total		7,823-7,865	10,615-10,657	11,673-11,757	15,169-15,253

---

[a] See Table 7-7.

[b] See Table 7-3; all quantities in terms of 100% pigment.

usage of eight diarylide pigments for the past 4 years. From 1975 through 1978, between 72 and 80% of all pigments of interest to this study (production plus imports) were consumed in ink making. The pigment yellows and some orange pigments are used extensively in inks, whereas the reds, blues, and certain orange pigments rarely find application in ink production.

The diarylide yellow pigments are of great economic importance in the printing ink industry. The major reasons for the widespread reliance on these pigments are the combination of high tinting strength (much higher than the Hansa yellows, pigments based on substituted anilines), good bleed resistance, almost perfect chromaticity for color printing, and excellent printing characteristics. According to industry sources, the lightfastness of Yellows 12 and 14 is only fair, and the rapid growth in consumption of Yellow 17 and Yellow 83 is partly due to their superior resistance to fading.

SOURCES OF PRODUCTION LOSS

In the manufacture of printing inks, material losses and waste generation are unavoidable. These sources of losses can be related to the basic steps in the production of printing ink.

Overall Losses

Many ink makers allow for an "overage" of 4 to 5%; that is, to mix a batch of 1,000 lb of finished product, sufficient resins, pigments and other additives will be employed to produce 1,040 to 1,050 lb of ink. This is a generous allowance for production losses and wastage; industry sources state that actual material lost in production is considerably less than 5% (Sutt, 1979; Barnett, 1979; Gilbert, 1979). Few plants, however, maintain detailed records of their losses.

Several ink plants were able to supply estimates of typical total production losses over the recent past:

1.5% (1973-1977)
4.0% (1977-1978)
2.6% (since 1970)
3.0% (1974-1976)
2.5% (last 20 years)
2.4% (1977)
Average: 2.7 lb per 100 lb of ink

These losses typically include all shrinkage from the purchase of raw materials to shipment of the finished ink. Individual sources of loss of ink ingredients were considerably more difficult to define; only a few production managers were able to estimate the incidence of broken shipping containers, spillage, off-specification materials not salvageable, clean-up residues, and end-of-run ink sent to waste.

The extent of production losses are markedly affected by such factors as batch size, type of ink produced (paste or liquid), the form of pigment used (dry toner or flushed color), solvent or water-base vehicle, type of production equipment, and the frequency and kind of cleaning system used (Sutt, 1979). Each of the sources of pigment or ink loss will be considered in turn for a typical (medium size) ink plant.

Weigh Station Losses

Dry diarylide toners are most commonly received in 25 or 50 lb plastic-lined shipping sacks, or in fiber drums. Ink makers estimate that from 1/4 to 1 oz may remain in the folds and crevices of sacks and drums after emptying into a mixing tub (Barnett, 1979; Vathako, 1979). MRI estimates that approximately 0.05 to 0.125% of organic pigments remain in the original shipping package. The ink industry recognizes that residues in shipping containers pose one of the biggest sources of material losses (Anon, 1979).

A few ink plants report the use of returnable shipping containers to reduce raw material losses and minimize contamination. At least one plant has installed a special "air pallet" system that uses shipping containers which fluidize finely divided materials to ensure almost complete discharge of the contents (Anon, 1978a).

Predispersed pigments (flushed colors, dry dispersions, and liquid dispersions) are much more widely used in the United States than in other countries (Patton, 1973). In 1977, only 2,961,000 lb (or 36.6%) of Yellow 12 or Yellow 14 were sold as dry, full strength color (Anon, 1978b). The balance was used as flushed colors (49.1%) and as aqueous dispersions, dry dispersions, or dry extended toner (14.3%). In using flushed colors there is no dust and little spillage. Usually the shipping containers are rinsed into the ink batches, so pigment loss in raw material handling is estimated to be 40% lower than for dry toners (Gilbert, 1979; Vanderhoff, 1979). MRI estimates that losses are approximately 0.075 to 0.10% of pigment content, mostly as container residues.

Losses in Ink Processing and Packaging

Depending on the type of inks being produced, there are several processing steps that generate wastes or pigment losses. Initial pigment dispersion is accomplished using high speed dispersers, sand mills, or quite commonly, a three roll mill. High speed, sawtooth dispersion mills can be used in the mixing tubs and the dispersion head washed into the batch after mixing. Hence, very little waste is associated with this type of dispersion. A few older plants use old style pebble mills to grind their inks. Where separate pebble mills are dedicated to use with one color of ink, virtually no waste occurs in the dispersion step, and the mills are only rarely cleaned out (Renson, 1979).

Roll mills and sand mills require cleaning before switching to a different color or pigment. Grinding on a three- or five-roll mill continues until a plate test for fineness of grind shows only one or two scratches. Quite frequently, the grind will be completed with 1 to 2% of the original mix still working at the feed roll. At this stage, the mill is stopped and the unground paste is removed (Barnett, 1979). Sometimes this paste can be added to the next similar batch, but among ink plants contacted, the most frequent practice was to place the residue in cans that are sent to ink waste (Vathako, 1979; Sutt, 1979; Barnett, 1979).

Mixing tubs used in ink making are cleaned with varying frequency and by several methods. All plants conduct some dry cleanup by wiping or scraping. Tubs can be rinsed with water, solvent or caustic, or some combination of methods. Water rinses are normally used following water base ink batches; solvent rinsing after oil base or solvent ink batches; and caustic rinsing may be used for either. Many plants routinely use caustic rinsing for smaller portable tubs and clean fixed tubs with caustic only when required because of heavy buildup of ink residue.

Batches of solvent base or oil base ink are usually rinsed with solvent and do not generate wastewater. The dirty solvent is generally handled in one of three ways:

1. Used in the next compatible batch of ink as part of the vehicle.

2. Collected and redistilled either by the ink plant or by an outside contractor for subsequent reuse or sale.

3. Reused as wash solvent with or without settling until considered spent, then sealed in drums for disposal. If a settling tank is used, the settled sludge is periodically removed for disposal as solid waste.

Plants that employ caustic washing systems clean the tanks and mixing tubs in several ways:

- Hot caustic from a holding tank is pumped through spray nozzles into the tub being cleaned and the caustic is returned to the holding tank.
- Tubs are filled with caustic wash and soaked until clean. The caustic is then transferred to the next tub to be soaked and eventually either stored for disposal or discharged as waste.
- Small portable tubs may be soaked in a caustic vat until clean or they may be washed in a machine like a large dishwasher which circulates hot caustic spray followed by a water rinse.

Both fixed tanks and portable tubs that are cleaned with caustic receive a water rinse. Rinse water is most commonly added to the caustic solution as makeup water, although some plants discharge rinse water to a sewer.

The quantity of water used to clean tubs in those plants that employ water rinsing is partly determined by the water pressure used in washing. Plants employing high pressure rinses tend to generate less tub cleaning wastewater per batch of ink (Burns and Roe, 1979a).

Sources of ink loss other than equipment cleaning vary widely among ink plants but often include residues from spills which may be hosed into floor drains; wastewater from cleaning tank trucks used to deliver raw materials; off-specification or spilled ink batches which cannot be reworked and are usually discharged as solid waste; residues from laboratory testing; wastewater from laundering shop rags that are used to clean ink tubs and other equipment; and ink washed from employees' hands.

The ink industry, as a whole, generates approximately 40,000 gal. of process wastewater daily, about 75% of which is actually discharged. The remaining water is reused in ink making, evaporated, or drummed for disposal as solid waste (Burns and Roe, 1979a).

After the initial dispersion of pigments and resins into the vehicle, ink batches are diluted to the required viscosity, checked and adjusted for tint, and the necessary additives are incorporated. Following this quality control step, the ink is ready for packaging or shipment. Larger ink making facilities may use packaging equipment to load ink into cans, tubs, or pails. Many plants, however, package inks directly from the ink mill. Because ink batches are normally initially formulated with sufficient raw materials to produce 4 to 5% excess ink that will be shipped, some residual ink remains at the end of packaging. Depending on the circumstances, these residues are added to the next batch or are drained into drums or holding tanks as waste ink (Barnett, 1979; Gilbert, 1979).

Based on discussions with ink production specialists and observation of ink making and equipment cleaning practices in typical plants, MRI estimates losses associated with the various processing and packaging steps as follows:

Paste Inks

. Oil base or solvent base, ink residue	1.5%
. Oil or solvent base, water or caustic wash	1.0%
. Water base, ink residue	1.0%
. Water base, water or caustic wash	3.0%

Liquid Inks

. Oil base or solvent base, ink residue	1.2%
. Oil or solvent base, water or caustic wash	1.0%
. Water base, ink residue	0.8%
. Water base, water or caustic wash	2.5%

WASTE HANDLING AND TREATMENT

Wastewater containing ink from floor and equipment cleanup is most commonly discharged to a sewer; no plants are known to discharge waterborne waste directly to a receiving stream (Burns and Roe, 1979a).

Less than 15% of all ink plants employ some form of wastewater treatment prior to discharge. Since these plants are typically the larger facilities, it is assumed that about 30% of all wastewater receives at least minimal treatment. The most common methods used by ink plants for pretreating wastewater prior to disposal are gravity separation or settling. A few plants also neutralize the caustic and skim water before discharge. Relatively few ink plants are known to employ sophisticated wastewater treatment. The number of ink plants that employ some form of wastewater treatment prior to discharge is shown in Table 9-5.

TABLE 9-5. WASTEWATER PRETREATMENT PRIOR TO DISCHARGE

Type of treatment	No. plants	Percent
Neutralize	9	2.0
Settle	36	7.8
Flotation	0	0
Polymer	0	0
Lagoon	3	0.7
Carbon adsorption	0	0
Equalization	3	0.7
Evaporation	11	2.4
Lime addition	0	0
Trickling filter	0	0
Primary gravity separation	19	4.1
Filtration	4	0.9
Alum addition	2	0.4
Activated sludge	7	1.5
Any form of pretreatment	30	13.0

Source: Appendix I - Questions 120 to 141 (Burns and Roe, 1979a).

Analysis of the wastewater from ink plants clearly shows the presence of the pigments generally used in inks. Typical data for wastewater from several plants are given in Table 9-6 (Burns and Roe, 1979a). Plant No. 7 did not treat wastewater. Plant Nos. 10 and 23 used only gravity sedimentation. Plant No. 22 used settling, neutralization and surface skimming of caustic wash and condensate from steam cleaning of ink tubs and tanks. Levels of barium, chromium, lead, and zinc indicate that the pigments are carried into the waste and washing water. Relatively simple gravity settling at Plant No. 22 shows the removal of 75% of total solids and somewhat higher removal of most heavy metal pigments.

All of the plants sampled used the diarylide pigments based on 3,3'-dichlorobenzidine as one of their raw materials. About 85% of all plants surveyed reported the use of various diarylide pigments:

- 69.1% used yellow toner
- 44.3% used orange toner
- 3.9% used yellow toner with copper
- 30.2% used nonaqueous diarylide dispersions
- 19.6% used yellow aqueous dispersions
- 6.1% used red aqueous dispersions
- 0.7% used orange aqueous dispersions

In the wastewater samples from ink plants, 3,3'-dichlorobenzidine was found in only one treated effluent sample at a concentration less than 10 μg/liter (Burns and Roe, 1979a). This finding is somewhat unexpected because the extensive dilution of ink residues in the wastewater should have been sufficient to reduce the levels of free 3,3'-dichlorobenzidine in diarylide pigments below the unit of detection. Diarylide pigments typically contain about 10 ppm of free 3,3'-dichlorobenzidine base as an impurity. The wastewaters, both raw and treated, showed total suspended solids concentrations (chiefly resins, pigments, and fillers) ranging from 200 to 800 ppm.

Since it is evident that ink plant wastewater contains traces of other pigments, failure to detect 3,3'-dichlorobenzidine in the effluent does not indicate that diarylide pigments are not present in the discharge.

For plants that do not discharge wastewater to a city sewer, the most common method of disposal is contract hauling. Nearly 34% of plants surveyed had wastewater and/or spent caustic sludges handled by contract hauling. Most contract haulers used by ink plants discharge the sludge to a landfill although a small number incinerate or reclaim the wastes (Bratchler, 1979).

Discussions with salvage haulers of ink plant wastes revealed that the vast majority of sludges and ink residues from ink plants find their way into

TABLE 9-6. ANALYTICAL DATA FROM INDIVIDUAL PLANT SITES
(Selected Compounds Only)

Parameter measured (all units μg/ℓ unless noted)	Plant number					
	7 (Batch No. 2)	10	23	22 (raw)	22 (treated)	% removal
pH	8.8	7.6	12.9	12.9	12.5	-
TS (mg/ℓ)[a]	11,840	3,900	1,100	22,600	5,600	75.2
TSS (mg/ℓ)[b]	1,310	480	120	1,600	110	93.1
Aluminum	30,000	2,000	1,000	20,000	600	97
Barium	30,000	900	500	20,000	100	99.5
Chromium	30,000	20,000	200	10,000	50	99.5
Molybdenum	6,000	1,000	100	700	50	92.9
Lead	40,000	50,000	4,000	90,000	200	99.8
Titanium	70	300	80	3,000	3,000	0.0
Zinc	3,000	600	1,000	1,000	1,000	0.0

Source: Appendix H. Burns and Roe, 1979a.

a/ TS = total solids.

b/ TSS = total suspended solids.

landfills (Taylor, 1979). Significant quantities of ink wastes from equipment cleaning are also discharged to sewer systems.

There is no evidence of airborne pigment dust emissions from ink making. Special tests for pigment dusts have been conducted in one ink production plant (MRI, 1979a). Sampling pumps were attached to the clothes of workmen at the pigment weighing station to determine whether the lead base pigments being used created a dust hazard. Neither lead nor chromium was detected. Because tests were being conducted, it is possible that greater care may have been exercised here than is typical in production plants. However, these tests and on-site observations by MRI in several ink manufacturing plants indicate that airborne pigment dust from raw material handling represents a negligible route of discharge to the environment.

ESTIMATED LOSSES

The flow chart in Figure 9-1 is an example of a materials balance for diarylide pigments in printing ink and is based on a consumption in 1978 of 15,253,000 lb, which is the maximum quantity of diarylide pigments believed to be used (production plus imports). Although 9.6 million pounds of flushed color and dispersions were used, compared to 5.6 million pounds of dry toner, pigment losses in shipping containers and weighing and handling losses are about equal for the two types of pigments. Total pigment losses prior to grinding are only about 14,000 lb/year.

Waste ink residues generated in ink processing, packaging, dry cleanup, and solvent washing are generally sent as solid waste in landfills.

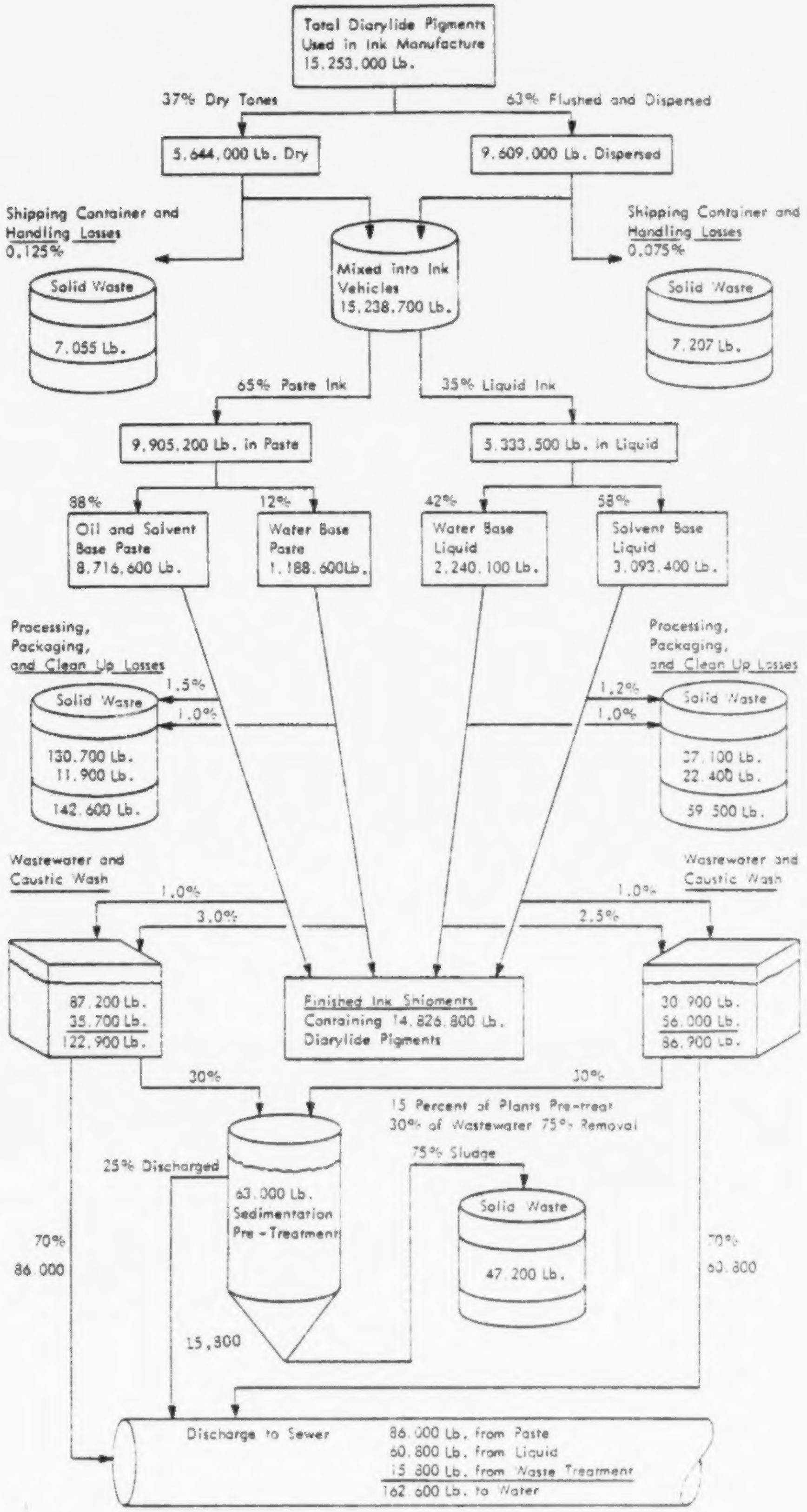
About 143,000 lb of residue and sludge pigments are generated annually from paste inks. Liquid inks are made in smaller volumes and also produce less waste; about 60,000 lb of pigments enter solid waste from this source.

Wastewater represents a major source of pigment discharge. Approximately 86,000 lb of pigment from paste ink making and about 61,000 lb of pigments from liquid ink waste are discharged to sewers. Of the total pigment load in wastewater (~ 210,000 lb/year), an estimated 30% is pretreated prior to discharge, with a removal efficiency of approximately 75% or more. From this treated wastewater, about 47,000 lb of pigments are contained in sludges disposed in landfills. An additional 16,000 lb/year is discharged with the treated wastewater. Of the initial 15.25 million pounds of diarylide pigments, about 14.83 million pounds of pigment (97%) is contained in finished inks sent to printing shops. These computed losses of 3% compare favorably with the mean overall ink loss rate of 2.7% reported by experienced ink makers.

A summary of the estimated losses of diarylide pigments for the period 1975 to 1978 is shown in Table 9-7. These estimated losses are based on pigment consumption ranges presented in Table 9-4.

INK LOSSES IN PRINTING

Following manufacture, printing inks are used primarily in commercial printing. The diarylide pigments of interest are used almost exclusively


Total Diarylide Pigments Used in Ink Manufacture 15,253,000 Lb.
37% Dry Tones
63% Flushed and Dispersed
5,644,000 Lb. Dry
9,609,000 Lb. Dispersed
Shipping Container and Handling Losses 0.125%
Solid Waste
7,055 Lb.
Mixed into Ink Vehicles 15,238,700 Lb.
Shipping Container and Handling Losses 0.075%
Solid Waste
7,207 Lb.
65% Paste Ink
35% Liquid Ink
9,905,200 Lb. in Paste
5,333,500 Lb. in Liquid
88%
Oil and Solvent Base Paste 8,716,600 Lb.
12%
Water Base Paste 1,188,600Lb.
42%
Water Base Liquid 2,240,100 Lb.
58%
Solvent Base Liquid 3,093,400 Lb.
Processing, Packaging, and Clean Up Losses
1.5%
1.0%
Solid Waste
130,700 Lb.
11,900 Lb.
142,600 Lb.
Processing, Packaging, and Clean Up Losses
1.2%
1.0%
Solid Waste
37,100 Lb.
22,400 Lb.
59,500 Lb.
Wastewater and Caustic Wash
1.0%
3.0%
Wastewater and Caustic Wash
1.0%
2.5%
87,200 Lb.
35,700 Lb.
122,900 Lb.
Finished Ink Shipments Containing 14,826,800 Lb. Diarylide Pigments
30,900 Lb.
56,000 Lb.
86,900 Lb.
30%
30%
15 Percent of Plants Pre-treat 30% of Wastewater 75% Removal
25% Discharged
63,000 Lb. Sedimentation Pre-Treatment
75% Sludge
Solid Waste
47,200 Lb.
70%
86,000
70%
60,800
15,800
Discharge to Sewer
86,000 Lb. from Paste
60,800 Lb. from Liquid
15,800 Lb. from Waste Treatment
162,600 Lb. to Water

Source: MRI estimates.

Figure 9-1. Sample Materials balance for diarylide pigments in printing inks in 1978.

TABLE 9-7. ESTIMATED LOSSES FROM THE PRINTING INK INDUSTRY

	Quantity (1,000 lb)[a]			
	1975	1976	1977	1978
Solid Waste				
Shipping container and handling loss	7.3	9.9	10.9-11.0	14.2-14.3
Processing, packaging, and cleanup	103.7-104.2	140.6-141.3	154.7-155.9	201.0-202.1
Sludge from wastewater	24.2-24.4	32.8-32.9	36.1-36.4	47.0-47.2
Subtotal solid waste	135.2-135.9	183.3-184.1	201.7-203.3	262.2-263.6
Air	b/	b/	b/	b/
Wastewater				
Caustic wash and water rinse; discharged without pretreatment	75.3-75.7	102.2-102.6	112.4-113.2	146.0-146.8
Effluent from pretreatment	8.1	11.0	12.0-12.1	15.7-15.8
Subtotal to water	83.4-83.8	113.2-113.6	124.4-125.3	161.7-162.6
Total pigment loss	218.6-219.7	296.5-297.7	326.1-328.6	423.9-426.2
Ink shipments (pigment content)	7,603.3-7,646.4	10,317.3-10,360.5	11,344.4-11,430.9	14,742.8-14,829.1
Total pigment use[c]	7,823.0-7,865.0	10,615.0-10,657.0	11,673.0-11,757.0	15,169.0-15,253.0

a/ All pigments used in printing inks are derived from 3,3'-dichlorobenzidine (DCB) except Orange 16, which is derived from 3,3'-dimethoxybenzidine. Since Orange 16 contributed only 1.1-1.5% of the total quantity in any one year from 1975-1978, it is included with the DCB pigments and not presented separately.

b/ Minute quantities.

c/ See table 9-4.

in process color printing, printing colored materials used in packaging, newspaper supplements, and specialty color reproduction processes.

Regardless of the printing process, certain types of ink losses have been identified:

- Ink not removed from shipping containers;
- Ink from supply fountains;
- Press and plate washing;
- Press overruns and misruns; and
- Trim, broke and waste.

Little or no airborne pigment loss occurs even with steam or heat-set inks. Most color printing plants are carefully controlled in terms of temperature, humidity, and ventilation; exhaust air is often minimal.

Minor amounts of ink enter wastewater from the cleaning of equipment using water based printing inks. For those classes of printing processes, the volume of ink removed in washing equipment is generally less than 1% of ink consumption. Printing companies contacted reported that wash-water from equipment cleaning was very often discharged into city sewers (Peters, 1979; Fagan, 1979; Schafer and Bastin, 1979). A limited survey did not find any printing shop having any type of special treatment or disposal methods for ink contaminated washwater.

The majority of the ink discarded or wasted in printing is placed in trash containers and handled as commercial solid waste. Ink cans, containing residues not readily removed by spatulas or draining, are discarded in the trash. This is said to represent by far the largest single loss of ink in most printing plants (McGrew, 1979). Small ink cans (1 to 5 lb) typically contain from 10 to 55 g of ink when discarded, averaging 2.3%. Tubes and cartridges retain up to 20 g when empty and thrown away. Larger ink containers are estimated to have residues of about 1.5% of the original contents, or up to 3/4 lb in a 50-lb pail. Fluid inks used in gravure and some flexographic processes were found to have residues in the range of 1 to 2 fl oz/gal. or 0.8 to 1.6%, which is comparable to losses with larger size cans of paste ink. Hence, discarded ink in containers may range from about 1.5 to 4.4% of purchases (MRI, 1979b).

With paste inks, some ink skinning and splatter occur at the ink supply fountains. Small quantities are periodically removed with spatulas or wiped up with shop wipes and thrown into trash drums. Printers estimate that up to 1% of paste ink is lost through this route (Fagan, 1979). Fluid ink losses are lower. When standard process colors are used, ink fountains may require complete cleaning out only once each week. Ink removed from press cleaning and fountain cleaning is estimated to account for 1.5 to 2.7% of ink purchased. All plants contacted reported that these cleaning wastes were either placed in general trash, or temporarily stored in safety cans before being emptied into plant trash (Schafer and Bastin, 1979).

The printing waste allowance varies with the type of press operation and the nature of the material being printed, but is always substantial. Sheet-fed color lithography often allows for the spoilage or discard of 500 sheets from a standard 3,600 sheet run (12.2%) (Peters, 1979). The U.S. Government Printing Office reported that the built-in losses often run close to 20 to 25% for broke, trim misruns, and overruns (Materozzi, 1976). A few large establishments separate out recoverable paper waste for recycling, but most smaller printing plants treat printing waste as general trash to be hauled away by commercial waste firms.

Since the preponderance of printing ink lost in printing enters the solid waste stream, losses may be summarized as:

Discarded in ink containers	1.5 to 4.4%
Removed in press cleaning	1.5 to 2.7%
Discarded as printing waste	9.5 to 13.0%
	12.5 to 20.1%

Wastewater discharge originating from cleanup of water base ink printing machines is estimated to contain ~ 2% of the water base printing ink. In 1978, ~ 3.3 million pounds of diarylide pigments were used in water base inks, which means waterborne discharge is approximately 66,100 lb annually.

POSTPRINTING DISPOSITION

The useful life of printed matter is fairly short. The bulk of diarylide pigments are consumed in printing newspaper supplements, magazines, advertising matter, catalogs, and packaging. It is assumed that 90% of these printed materials are discarded within 1 year after printing.

Waste paper recycling is currently limited except for newsprint and corrugated boxboard. About 3.1 million tons of newsprint were recovered in 1977 or about 30% of total production (Franklin et al., 1979). Of the 22 million tons of boxboard produced, 7 million tons were reclaimed. Only about 4% of newsprint is deinked in recycling and none of the corrugated is deinked. Recycled paper is used primarily in paperboard packaging, gypsum board, and some tissue products.

Most of these products have a short life cycle and are ultimately disposed in mixed solid wastes. Since 1975 approximately 93% of mixed solid wastes have been landfilled; currently only about 7% is incinerated. Using the ink and printing waste factors estimated in this section and an assumed discard rate of 90%, the estimated fate of diarylide pigments in printed materials is summarized in Table 9-8.

TABLE 9-8. ESTIMATED FATE OF DIARYLIDE PIGMENTS IN PRINTED MATERIAL

	Quantity (1,000 lb)			
	1975	1976	1977	1978
Total pigment employed (see Table 9-7)	7,603-7,646	10,317-10,361	11,344-11,431	14,743-14,829
Wastewater loss				
Cleanup of water-base ink (~2% loss)	33.9-34.1	46.0-46.2	50.6-51.0	65.8-66.1
Solid waste loss				
Container residue (1.5-4.4%)	114-336	155-456	170-503	221-652
Press loss (except water-base) (1.5-2.7%)	114-206	154-279	169-307	220-399
Printing waste discard (9.5-13.0%)	722-994	980-1,347	1,078-1,486	1,401-1,928
Printed material disposition				
Prompt waste	950-1,536	1,289-2,082	1,417-2,296	1,842-2,979
Discarded within 1 yr (90%)	5,430-5,996	7,370-8,123	8,097-8,967	10,528-11,629
Landfilled (93%)	5,050-5,576	6,854-7,555	7,530-8,339	9,791-10,815
Incinerated (7%)	380-420	516-569	567-628	737-814

SECTION 10

PAINT AND COATINGS INDUSTRY

INDUSTRY CHARACTERISTICS

Paint, varnish, lacquer, and other protective coatings are manufactured domestically in approximately 1,400 establishments operated by about 1,300 companies. Total industry employment is 65,000, of which approximately 36,000 are involved in paint production. The 1972 Census of Manufactures showed 1,599 establishments, 687 of which had more than 20 employees.

A recent survey of the paint and coatings industry obtained responses from 1,374 establishments (Burns and Roe, 1979b). The geographic distribution of paint manufacturing plants obtained from this survey shows the larger paint plants tend to be concentrated in major centers of manufacturing and population. Approximately 45% of all plants having more than 100 employees are located in just four states (New Jersey, Illinois, Ohio, and California). The states containing the major percentage of all paint plants are shown in Table 10-1.

The principal products of the paint industry (SIC 2851) are consumer paint products called "trade sales," which are sold primarily off the shelf for exterior and interior painting of buildings, and industrial finishes sold to manufacturers for factory application to products such as automobiles, furniture, appliances, and machinery.

The output of the paint industry in 1977 was approximately 1 billion gallons of product valued at slightly more than $4 billion. Growth in paint production is modest, about 3% annually in volume and about 5% annually in value of shipments (Census, 1977).

PAINT MANUFACTURING

Production Processes*

Paints can be classed as either solvent base or water base (also called latex base), but there is little difference in the production processes used.

---

* This brief characterization of paint production processes, focusing upon pigment usage, sources of waste and equipment cleaning practices, is based in part on a recent report on the paint manufacturing industry (Burns and Roe, 1979b).

TABLE 10-1. DISTRIBUTION OF LARGE PAINT PLANTS, BY STATE

State	% of all paint plants
Illinois	7.7
California	14.3
New Jersey	8.2
Ohio	7.5
New York	7.9
Pennsylvania	4.8
Texas	4.2
Michigan	3.4
Missouri	3.7
Georgia	2.5
Indiana	2.5
Kentucky	1.6
North Carolina	1.5
All others	31.2
Total	100

Source: Burns and Roe (1979b).

The major production difference is in the carrying agent; solvent base paints are dispersed in an oil mixture, while water base paints are dispersed in water with a surfactant used as the dispersing agent. Another significant difference is in the cleanup procedures used. As the water base paints contain surfactants, it is much easier to clean up the formulating tanks with water. The tanks used to make solvent base paint are generally cleaned with an organic solvent, but cleaning with a strong caustic solution is also a common practice (Barrett, 1973; EPA, 1973).

Major raw materials used in paint manufacture in terms of pounds consumed are oils, resins, pigments, and solvents. Alkyls and drying oils, such as linseed oil, are used as the film forming binder in some solvent base paints. Semidrying oils and water soluble alkyls are used in the manufacture of water base paints.

Pigments are used to impart opacity and color to the coatings. The four basic types of pigments are: (a) prime white pigments, such as titanium dioxide and zinc oxide, (b) colored inorganic and organic pigments, (c) filler and extender pigments, and (d) metallic powders.

Practically all paints are produced using a batch process. The major difference in the size of a paint plant is in the size of the batches. A small paint plant will produce batches from 100 to 500 gal. while a large plant will manufacture batches up to 6,000 gal. In general, there are too many color formulations to make a continuous process feasible.

Solvent Base Paint Operations--

There are three major steps in the solvent base paint manufacturing process: (a) mixing and grinding of raw materials, (b) tinting and thinning, and (c) filling operations. The flow diagram in Figure 10-1 illustrates these steps.

The mixing and grinding of raw materials for solvent base paints are accomplished in one production step. For high gloss paints, the pigments and a portion of the binder and vehicle are mixed into a paste of a specified consistency. This paste is fed to a grinder, which disperses the pigments by breaking down particle aggregates rather than by reducing the particle size. Two types of grinders are ordinarily used for this purpose: pebble or ball mills, and roll-type mills. Other paints are mixed and dispersed in a mixer using a saw-toothed dispersing blade commonly referred to as a high speed disperser.

In the second production stage, the paint is usually transferred to tinting and thinning tanks by gravity feed or occasionally by means of portable transfer pumps. At this stage, the remaining binder and liquid, along with various additives and tinting colors, are incorporated. The paint is then tested and the composition is adjusted as necessary to obtain the correct specifications for the type of paint being produced. The finished product is then transferred to a filling operation where it is filtered, packaged, and labeled (EPA, 1976; Barnett, 1979).

The paint remaining on the sides of the tanks may be allowed to drain naturally and the residue, or clingage as it is called, may be cleaned from the sides with a squeegee during the filling operation until only a small quantity of paint remains. The final cleanup of the tanks generally consists of flushing with a solvent until clean. The dirty solvent is treated in one of three ways: (a) it is used in the next paint batch as a part of the formulation; (b) it is placed in drums that are sold to a company where it is redistilled and resold; or (c) it is collected in drums with the cleaner solvent being decanted for subsequent tank cleaning and returned to the drums until only sludge remains in the drum. The drum of sludge is then sent to a landfill for disposal (Hine, 1971, Barnett, 1979; EPA, 1976).

Some plants clean solvent base paint tanks and equipment with hot caustic either on a regular or periodic basis. The caustic is generally recycled and is followed by a water rinse. Part of this water is returned to the caustic tank as makeup, and any remaining water is disposed of by (a) discharging to the sewer, (b) holding, treating, and discharging to a sewer, (c) drumming and landfilling, or (d) reusing as rinse water (Bruhns, 1971). In plants that manufacture both solvent base and latex base paints, this rinse water is often combined with the wastewater from latex base paint operations.

Water Base Paint Operations--

Water base paints are produced in a slightly different manner from solvent base paints. The pigments and extending agents do not require grinding because they are received in proper particle size. Hence, the dispersion of

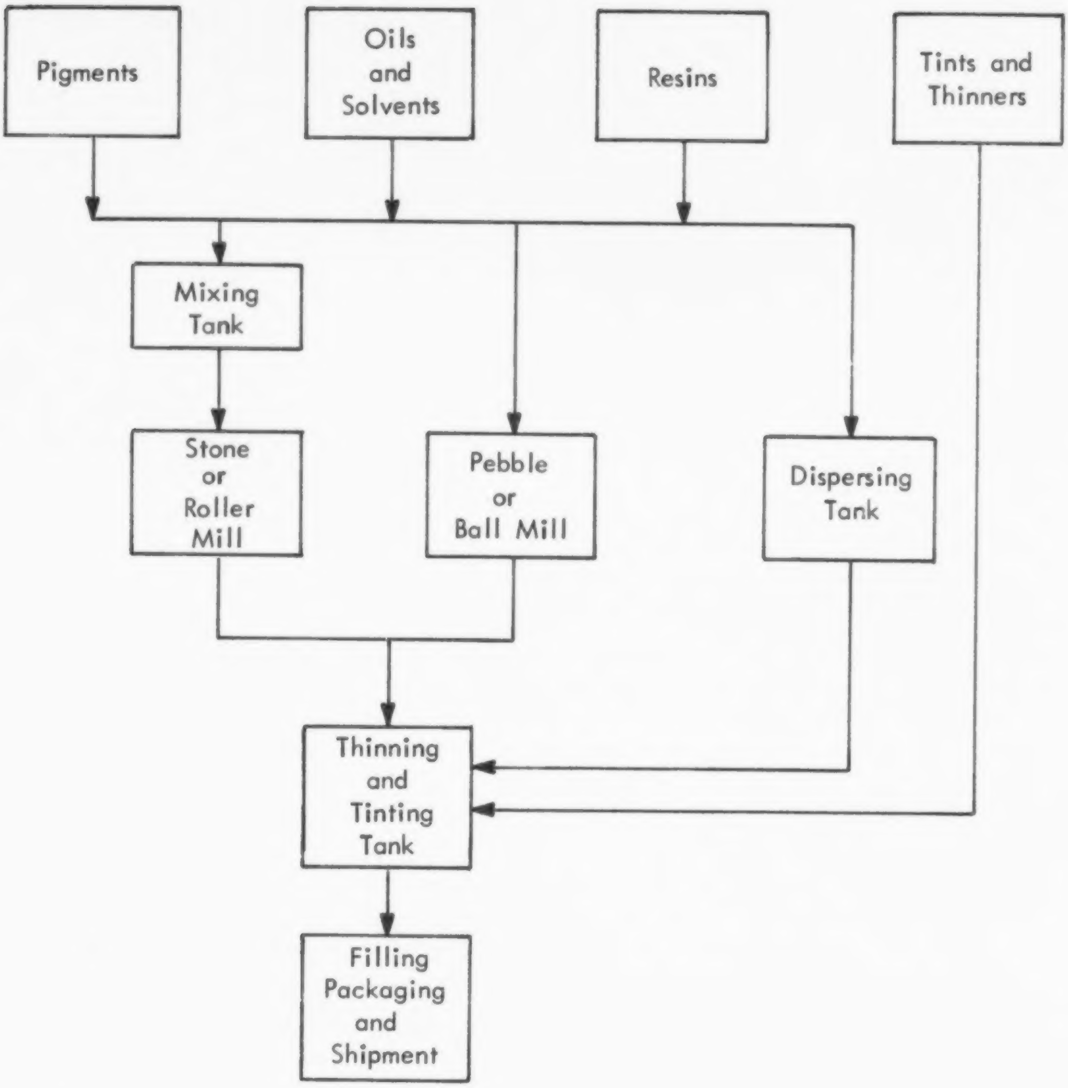

Pigments
Oils and Solvents
Resins
Tints and Thinners
Mixing Tank
Stone or Roller Mill
Pebble or Ball Mill
Dispersing Tank
Thinning and Tinting Tank
Filling Packaging and Shipment

Figure 10-1. Flow diagram of solvent base paint manufacturing process.

the pigment, surfactant and binder into the vehicle is accomplished with a saw-toothed high speed dispenser. In small plants, the paint is thinned and tinted in the same tank, while in larger plants the paint is transferred to special tanks for final thinning and tinting. Once the formulation is correct, the paint is transferred to a filling operation where it is filtered, packaged, and labeled in the same manner as for solvent base paints. The production process for water base paints is diagrammed in Figure 10-2.

As in the solvent base paint operation, as much product as possible may be removed from the sides of the tub or tank before final cleanup starts. Cleanup of the water base paint tubs is done simply by washing the sides with a garden hose or a more sophisticated washing device. The washwater may be: (a) collected in holding tanks and treated before discharge; (b) collected in drums and taken to a landfill; (c) discharged directly to a sewer; (d) reused in the next paint batch; or (e) reused in the washing operation (Miller, 1979).

Some paint plants may regularly or occasionally rinse latex base paint tanks and equipment with hot caustic in a similar manner to that described for solvent base paints. Any rinse water generated is combined with the regular cleanup water and disposed of by one of the same methods.

PIGMENT USAGE

The pigments used in paint production cover a wide range of materials. One medium size manufacturer reported that they maintain over 8,000 paint formulations on a computer listing, and annually manufacture more than 4,500 different production formulas, many of which differ primarily in pigmentation (Johnson, 1979).

Inorganic pigments are most widely used in white and tint base paints; barium, titanium, calcium, and zinc pigments are prominent in this class of product. Inorganic pigments also tend to dominate the colored paint field because they are more stable and less expensive than most organic toners. Inorganic extender pigments, such as the silicates, are also widely used in both white and colored coatings.

Data from a recent study show that the paint industry relies heavily on inorganic pigments. Half of the plants that responded to a survey indicated that they use over 70% inorganic colorants (Burns and Roe, 1979b).

Diarylide Pigments

The pigments derived from 3,3'-dichlorobenzidine and 3,3'-dimethoxybenzidine represent a small portion of all pigments used in the paint industry. This small usage of the diarylide pigments is fairly widespread--roughly one-third of all plants.

The paint industry accounts for less than 6% of the total consumption of diarylide pigments. Diarylide pigments tend to be more widely used in solvent base coatings than in water base paints; and more extensively in industrial coatings than in trade sales products, as shown in Table 10-2. The table

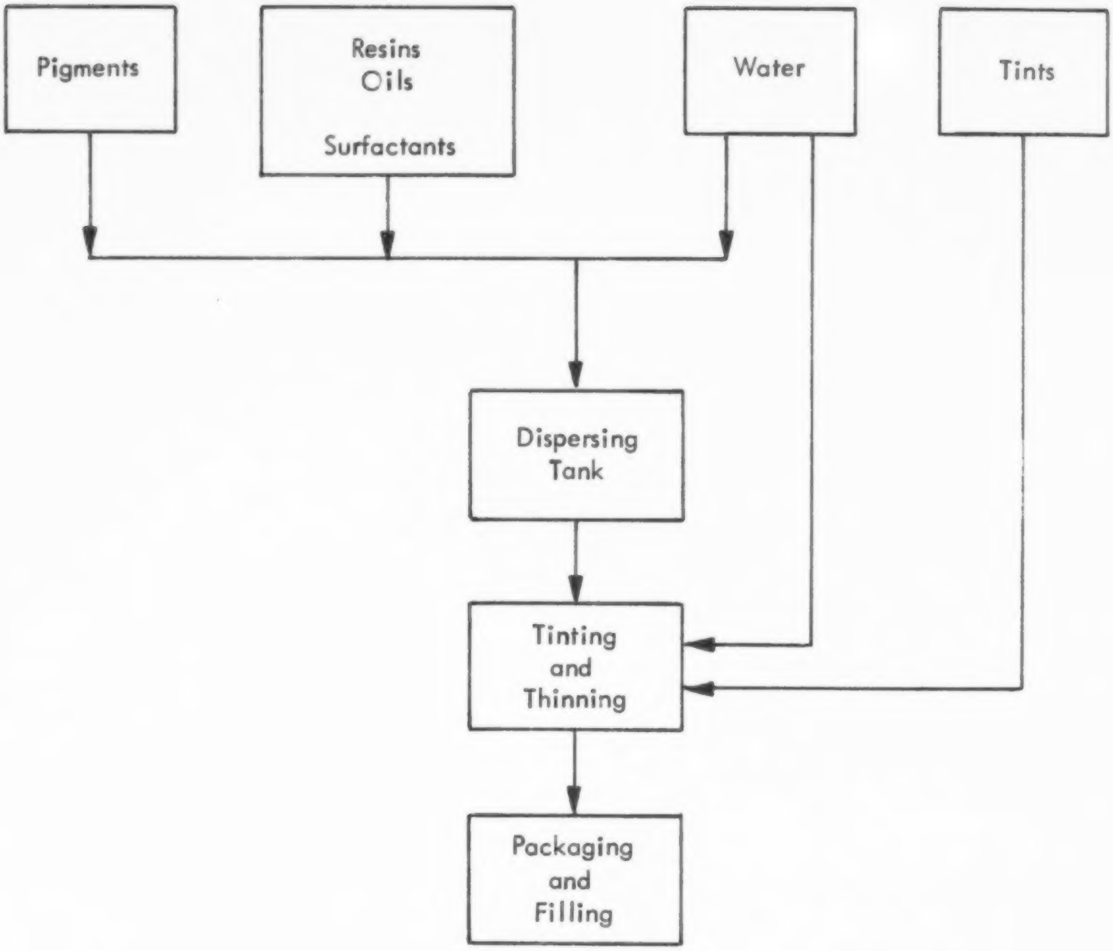

Pigments
Resins
Oils
Surfactants
Water
Tints
Dispersing Tank
Tinting and Thinning
Packaging and Filling

Figure 10-2. Flow diagram of water base paint manufacturing process.

TABLE 10-2. DIARYLIDE PIGMENTS IN PAINT PRODUCTION

Plant characteristics	Diarylide pigments usage Number of plants	Percentage
All plants	412	30
Paint production		
90+% solvent base	156	34
90+% water base	19	17
Paint sales		
90+% industrial	167	37
90+% trade	62	18

Source: Burns and Roe, 1979b.

shows that the use of these pigments is twice as frequent among solvent paint producers as it is for water base paint producers and twice as common in industrial paints as in consumer paints.

Usage of diarylide pigments in exterior paints is limited because most of these pigments fade in sunlight. Although some diarylide pigments are used in tinting interior latex paints, the inorganic color pigments (such as inorganic oxides or the titanated pigments) are more generally used because they perform well and are less costly. Diarylide pigments find their greatest application in brightly colored lacquers, enamels and specialty coatings where high tinting strength and color saturation are desired. The use of diarylide pigments allows production of bright coatings with high hiding power at relatively low pigment loadings. This is a characteristic of considerable value in some industrial finishes and consumer products, such as aerosol spray enamels.

The approximate consumption of diarylide pigments by the paint industry is estimated in Table 10-3. These estimates by MRI are based on discussions with pigment sales departments, the purchasing agents and formulation specialists for six diversified paint producers, and available statistics on pigment consumption (Byrd, 1979; Richardson, 1979; Miller, 1979; Asher, 1979).

Annual consumption of diarylide pigments in paints is estimated to account for approximately 6% of total diarylide pigment consumption. The pigment based toners are seldom, if ever, used as the sole color pigment; they are usually used to enhance the saturation and chroma of other pigments. The paint industry relies far more heavily on inorganic colors. Over 62% of plants use chrome yellow, compared with 10.5% using yellow toners. Some 52% report use of molybdate orange, versus 22% using Oranges 13 and 16. The

TABLE 10-3. ESTIMATED DIARYLIDE PIGMENT CONSUMPTION IN PAINTS

Pigment	Quantity (1,000 lb)[a] 1975	1976	1977	1978
Yellow 12	182	236	261	356
Yellow 13	17	28	26	36
Yellow 14	19	30	32	31
Yellow 17	125	230	300	343
Yellow 83	63-75	89-96	92-112	111-131
Orange 13	11	14	12	12
Orange 16	23	29	26	28
Red 38	48-49	51	51	53-54
Red 41	0.4-0.6	0.4-0.6	0.4-0.6	0.4-0.6
Blue 25	7	6-7	6	5-6
Total	495-507	710-722	806-827	975-998

Source: MRI estimates.

[a] Quantities derived from Tables 4-3 and 4-6.

phthalocyanine blues and greens are among the more widely used organic pigments; nearly 60% of paint plants use these pigments (Burns and Roe, 1979b). Use of diarylide pigments in aqueous and nonaqueous dispersions is small but significant, with about 6% of all plants employing these predisposed colors. Nonaqueous dispersions or flushed toners are employed more than aqueous dispersions. This is probably due to less demand for intense coloration in water base paints. Table 10-4 presents a comparison of the frequency of usage of different types and classes of pigments.

ESTIMATED LOSSES IN PAINT MANUFACTURE

In the manufacture of paint several principal sources or points exist at which pigments or pigment-containing paint can enter waste streams and possibly be discharged to the environment.

* Shipping container residues and pigment handling loss.

* Spills of product.

* Solvent washing and cleanup.

* Water or caustic equipment cleaning.

* Overage or packaging residues.

Other minor sources of discharge include laboratory paint samples and residues, laundering of shop cloths used in cleanup, cleaning of truck tanks of incoming raw materials, and production work hand washing (Mellan, 1979; Asher, 1979).

The levels or magnitude of losses throughout production and cleanup are directly affected by factors which include size and scale of operations, specialization in water base or solvent paints, use of dedicated tanks and equipment, type of equipment cleaning practiced, and the availability of suitable waste disposal systems. No satisfactory data were found from which the industry norms for loss rates could be derived. It was necessary, therefore, to obtain estimates of the probable range of losses from a number of experienced paint production managers. The consensus among 11 producers of both solvent and water base paints resulted in estimates for overall industry loss factors for the principal sources identified as follows:

* Pigment shipping container residues, plus spills and loss in pigment handling and weighing--0.2%; all treated as solid wastes.

* Processing and packaging waste in solvent base coatings, including off specification or spoiled batches that are not reused in subsequent paint batches--0.8 to 1.4%, average 1.0%. Over 80% treated as solid residue from solvent recovery or discard; 20% maximum may enter wastewater system, of which less than half will be discharged with treatment.

TABLE 10-4. RELATIVE USAGE OF COLOR PIGMENTS BY PAINT PLANTS

A. Inorganic color pigments	Percent usage	B. Organic pigments	Percent usage	C. Organic pigment dispersant	Percent usage
Zinc yellow	46.1	DCB orange toner	22.1	DCB yellow non-aqueous	5.9
Cd yellow-orange	11.6	DCB yellow toner	10.5	DCB yellow aqueous	5.5
Antimony Pb or Zn yellow	4.4	Pyrazalone red	4.2	DCB orange aqueous	3.7
Chrome yellow	62.4	DCB yellow with Cu	1.7		
Chrome orange	13.0	DCB yellow with Ni	11.4	Compare with:	
Molybdate orange	52.5	Phthalocyanine blue	57.9	Lead or chrome yellow non-aqueous	25.1
Lead yellow or red	29.0	Phthalocyanine green	56.2	Lead or chrome orange non-aqueous	21.6
Cd red	13.0			Lead or chrome green non-aqueous	10.8
Iron blue	39.5			Green (Cu or CN) non-aqueous	38.4
Chrome blue	2.0			Blue (Cu or CN) non-aqueous	38.3
Cd blue	0.7				
Silver blue	15.1				

Source: Burns and Roe, 1979b.

- Processing, packaging, and waste in water base paint may exhibit lower levels of losses because the batch sizes tend to be considerably larger--0.6% average. At least 75% enters wastewater, while the balance is handled as solid waste. Approximately half the water containing paint residues is recycled; the remaining half of these wastes will be discharged in wastewater with or without treatment.

- Solvent washing of equipment for oil and solvent base coatings accounts for 1.0 to 1.5% overall losses, average 1.2%. All of these residues eventually are handled as solid waste.

- Water or caustic washing of equipment used for either solvent or water base paints carries away 1.6% of production. About 30% of water wash is reused in paint. All caustic and the balance of water wash becomes wastewater.

- Miscellaneous losses are estimated to account for less than 0.1% of production; half solid, half wastewater.

- The diarylide pigments of interest are estimated to be consumed 65 to 80% in solvent base coatings.

Determination of paint losses is complicated considerably by the diversity of equipment cleaning practices used. Both solvent washing and water washing are extensively employed. The use of caustic cleaning is significant but is much less commonly used than in the printing ink industry.

The study by Burns and Roe (1979b) presents information on the distribution of tank cleaning methods within the paint industry (see Table 10-5). Most of the large plants that produce only water base paints use water washing as virtually the only cleanup technique. When making latex base paints on a large scale, most producers report that all of the wash water cannot be reused in paint making. Even with effective preservatives and biocides, the risk of biological contamination is so great that only washing residues from certain stages of production can feasibly be reused (Walanski, 1979). Further, the volumes of water wash employed in specialized latex paint plants is quite large. For these reasons, most large latex paint plants have constructed some type of wastewater treatment system. A small number of water base paint plants report that they have been able to operate without generating any wastewater. Table 10-6 compares the wastewater production of solvent base and water base plants. The plants making water base paint generate, on the average, about 1,650 gallons per day (gpd); solvent base plants typically generate about 1,700 gpd. Actual discharge of wastewater follows a different pattern. Over two-thirds of the solvent base paint plants did not discharge any water. The remaining one-third of plants had an average discharge of 2,600 gpd. Those water base paint plants that discharge water averaged 1,360 gpd or about 82% of wastewater generated.

Small plants are much more likely than large plants to reuse wastewater as part of product formulation. Only 1.1% of the large plants indicated reusing wastewater in product all of the time versus 16% of small plants and 13% of all plants that use a water rinse.

TABLE 10-5. METHODS OF TANK CLEANING

Rinsing method	Number of plants surveyed	Percent of plants
Water rinse only[a]	143	10.4
Solvent rinse only[a]	383	27.9
Caustic rinse or soak only[a]	14	1.0
Dry cleaning only	24	1.7
Water and caustic rinse[a]	30	2.2
Water and solvent rinse[a]	491	35.7
Solvent and caustic rinse[a]	40	2.9
Water, solvent and caustic[a]	187	13.6
Not answered	62	4.5
Total using:		
Water	851	62
Solvent	1,101	80
Caustic rinse	163	12
Caustic soak	164	12
Dry cleanup	189	14

Source: Burns and Roe, 1979b.

[a] With or without dry cleaning of tanks.

TABLE 10-6. VOLUME OF WASTEWATER GENERATED BY PAINT PLANTS

Wastewater generated (gpd)	Plants producing over 90% water base paint (%)	Plants producing over 90% solvent base paint (%)
0	11.0	44.7
1-100	56.9	21.1
101-500	9.2	6.3
501-1,000	2.8	2.6
1,001-6,000	11.9	4.4
6,001-12,000	-	1.7
Over 12,000	4.6	5.4
Not answered	3.7	13.7
Total	100.0	100.0

Source: Burns and Roe (1979b).

Wastewater from paint plants is infrequently discharged directly. The most widely used methods of disposal are discharge to city sewer, contract hauling, evaporation, and landfill or impoundment (EPA, 1976; Bruhns, 1971).

Some type of treatment or pretreatment of wastewater prior to discharge is used by 355 plants (Burns and Roe, 1979b). Settling and gravity separation are most commonly used. Some of the larger plants, especially those producing mostly water based paints, have installed physicochemical treatment systems. Advanced treatment with coagulants to aid precipitation of suspended matter typically shows greater than 95 to 98% removal of total suspended solids and 60 to 85% removal of metals found in pigments (Desoto, 1974).

Analysis of wastewater from paint plants shows the presence of pigments. Barium, cadmium, chromium, copper, molybdenum, lead, and titanium are almost always found in raw wastewater and at reduced levels in most treated discharge. No samples of wastewater tested were found to contain benzidine or 3,3'-dichlorobenzidine. Failure to detect 3,3'-dichlorobenzidine in wastewater from paint plants does not mean that diarylide pigments are absent.

Estimates for diarylide pigment losses and disposition from paint manufacture were derived from data on total diarylide toner use in paints together with loss factors supplied by industry (see Table 10-7). Largely because the diarylide pigments are used more in solvent base and industrial finishes

TABLE 10-7. ESTIMATED PIGMENT LOSS FROM PAINT MANUFACTURE - 1978

	Diarylide pigment consumed in paints[a] (975,000-998,000 lb)	
Source of loss	70% Solvent base 682,500-698,600	30% Water base 292,500-299,400
Shipping container and pigment handling	0.20% - solid	0.20% - solid
Processing and packaging	0.8 - 1.4% - 80% solid 20% water	0.60% - 25% solid 75% water[b]
Equipment cleanup	1.0 - 1.5% - solid	1.60% - 80% washwater[c] 20% caustic wash
Miscellaneous sources	0.1% - 50% solid 50% water	0.1% - 50% solid 50% water
Summary of losses		
Solid waste	1.9 - 2.9%	0.4%
lb	12,968 - 20,259	1,170-1,198
Water waste	0.2 - 0.3%	1.5%
lb	1,365 - 2,096	4,388-4,491 (3,072-3,144)[d]

Total losses: Solid waste -- 14,138 - 21,457 lb
Water waste -- 4,437 - 5,240 lb

Total paint shipment: 948,303 - 979,425 lb which generally employ solvent cleanup methods, the largest fraction of pigment residue is discarded as solid waste. The distribution of diarylide pigments associated with paint manufacture for 1975 to 1978 is shown in Table 10-8. Estimations employed in these calculations were presented earlier in this subsection. Using these industry estimations, the following percentages can be computed. Of the total quantity of pigment employed in solvent base paints, 1.9 to 2.9% (2.4% average) is disposed as solid waste, 0.2 to 0.3% (0.25% average) is discharged in wastewater, and 96.7 to 97.9% (97.3% average) is contained in paint shipments. For pigments in water base paints, 0.4% is disposed as solid waste, 1.5% is discharged in wastewater, and 98.1% is contained in paint shipments.

---

[a] See Table 10-3.

[b] Of the losses during processing and packaging of water base paints, 25% are solid waste and 75% are in wastewater. Fifty percent of the wastewater is recycled and 50% discharged without further treatment.

[c] 30% - recycled; 70% - discharged.

[d] 70% discharged with no treatment; 30% treated to achieve 75% solid removal. The solid removal figure is not included in the total range for solid waste.

TABLE 10-8. ESTIMATED PIGMENT LOSS FROM PAINT MANUFACTURE

Loss category	Quantity (1,000 lb)			
	1975	1976	1977	1978
Maximum total consumption[a]	495-507	710-722	806-827	975-998
Pigment discharged in wastewater[b]	2-3	3-4	~4	4-5
Pigment in solid waste[b]	7-11	10-16	12-18	14-21
Pigment contained in paint shipments[c]	481-498	690-709	784-811	949-980

a/ See Table 10-3.

b/ See Table 10-7 for percentage losses from solvent base and water base paints.

c/ Quantities obtained by difference.

LOSSES IN PAINT APPLICATION

The application of protective coatings is accompanied by significant losses due to unused paint, overspray, drop and spillage, and the cleaning of equipment used to apply the coating. The fraction of paint usefully applied to the intended surface may range from less than 75% for unskilled brush painting to more than 90% for electrocoating and industrial fused powder coating methods (Mullen, 1979). Hence, a substantial proportion of pigments used in paint making do not enter the environment directly because they are contained in surface coatings which have a useful life of several years.

Of the total quantity of diarylide pigments in paint shipments, approximately 30% are incorporated into water base paints and 70% into solvent base paints. Within the water base category, 28% are industrial sales and 72% are trade sales. For solvent base paints, 29% are trade sales, 62% are industrial sales, and 9% are other sales, which includes powder coatings, electrodeposition, dip coating, and other special application techniques. The distribution among the sale categories is accurate to ± 5%. However, within each of the sale categories, it is difficult to estimate painting losses with any degree of accuracy. Industrial coating operations using solvent base materials generally achieve a coating efficiency of 80 to 85% (Hahn, 1979). Makers of industrial painting equipment estimate that 8 to 10% of paint purchased is disposed of as solid residue and overspray collection, with another 7 to 10% collected in water curtain or scrubbing systems or through water washing (Maas, 1972). Most large industrial coating operations that generate waterborne paint wastes employ some type of concentration and treatment before discharging wastewater. MRI estimates that roughly 35% of industrial water contaminated with paint is treated at a removal efficiency of 75%. Sludges are widely removed by contract hauling. For trade sales of solvent base coating, the coating efficiency is estimated to be about 65 to 80% with approximately 15 to 25% discarded as solid waste and the remainder discharged as water waste. Other solvent base paint applications are estimated to show about 90% coating efficiency, with approximately 8% of the residue as solid waste and 2% as water waste.

Only wide approximations could be made for painting losses from water base industrial sales or trade sales. An approximate coating efficiency of 70 to 85% was assumed for both areas. Solid waste was estimated at 5 to 15% and water waste at 10 to 15%.

A summary of estimated diarylide pigment losses resulting from paint application processes is presented in Table 10-9.

TABLE 10-9. ESTIMATED PIGMENT LOSS FROM PAINT APPLICATION

Loss category	Quantity (1,000 lb) 1975	1976	1977	1978
Total diarylide pigment (see Table 10-8)	481-498	690-709	784-811	949-980
Water base (30%)	144-149	207-213	235-243	285-294
Industrial sales	41-42	57-59	66-68	79-82
Trade sales	103-107	150-154	169-175	206-211
Solvent base (70%)	337-349	483-496	549-568	664-686
Trade sales	98-101	140-144	159-165	193-199
Industrial sales	209-216	299-307	340-352	411-425
Other	30-31	44	50-51	60-62
Pigment in coatings	355-423	508-601	579-688	684-824
Pigment in solid waste	40-71	58-104	67-117	80-139
Pigment in wastewater discharge	35-55	50-78	56-88	76-126

SECTION 11

TEXTILE PRINTING

This section describes the textile printing processes that employ pigments based on 3,3'-dichlorobenzidine, 3,3'-dimethoxybenzidine, and 3,3'-dimethylbenzidine. An overview of the textile industry was presented in Section 4; the reader is referred to that section for a detailed industry characterization. The brief industry characterization is followed by a discussion of textile printing processes, specific type and estimated quantities of diarylide pigment used, and an estimation of losses for this industry.

INDUSTRY CHARACTERIZATION

Except for losses of colored material as scrap when patterns are cut (10 to 20% depending upon the type of pattern and fabric width), most of the losses of the pigments are restricted to those in Major Group 22 of the Standard Industrial Code (SIC). Major Group 22 is comprised of about 6,000 manufacturing facilities (EPA, 1979b). The primary activities of this sector include receiving and preparing fibers; transforming these materials into yarn, thread, or webbing; converting the yarn or web into fabric or similar products; and finishing these materials at various stages of production.

Fiber is the basic raw material in textile manufacturing. The fibers used to form the fabric or web can be either natural or synthetic. Natural fibers include wool, cotton, jute, silk, and flax. Synthetic fibers are cellulosic (e.g., rayon, acetate) or noncellulosic (e.g., polyester, nylon, spandex).

PRINTING PROCESSES

There are three basic textile printing processes: roller printing, screen printing, and transfer printing. Screen printing may be further divided into rotary screen or flat bed screen printing. The estimated quantity of fabric printed by each process is presented in Table 11-1. There are also printing classifications based on the type of printing paste used in a process: (a) pigment printing uses a color paste containing insoluble colorants; (b) dyestuff printing uses a paste containing soluble colorants; and (c) thermosol treatment uses a disperse dye which is applied to paper or fabric and diffused into the fabric by means of heat or steam. The thermosol process is used primarily for dyeing of polyester fabric and does not employ bisazobiphenyl dyes. Processing of the fabric after it has been printed with the paste varies according to the classification of the colorant and the fibers which are used.

TABLE 11-1. ESTIMATED QUANTITY OF FABRIC PRINTED BY PROCESS (1975-1978)

	Fabric printed[a] (10^6 lb)			
Printing process	1975	1976	1977	1978
Rotary screen	458	505	557	614
Flat bed screen	298	301	302	301
Roller	199	215	232	251
Transfer	40	54	70	88
Total	995	1,075	1,161	1,254

[a] These data are based on 1976 estimates by RTI (1979). An 8% growth rate for total textile printing industry was applied (RTI, 1979), with the following estimates of changing market shares for the different processes: rotary screen - up 1% annually; flat bed screen - down 2% annually; roller - no change; transfer - up 1% annually (RTI, 1979).

The methods for printing colors are described in the following subsections. Figure 11-1 shows the typical printing process.

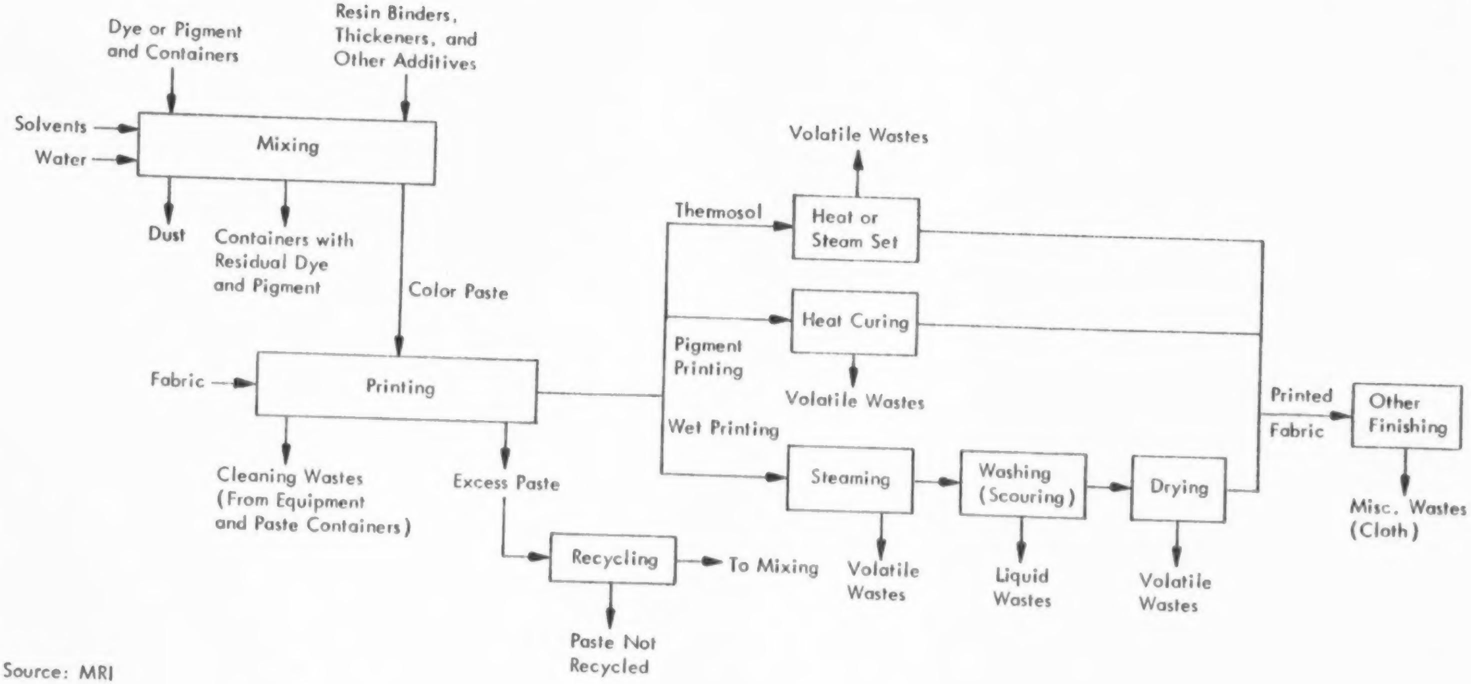
Roller Printing

Roller printing uses engraved rollers which are coated with the print paste. The paste is removed from the surface of the roller by a knife, called the color doctor, but paste is left in the engraved regions. This paste is then transferred by pressure to the fabric being colored. The equipment and material used in the process are a color pan to hold the printing pastes, a furnishing roller to transfer the paste from the color pan to the engraved roller, the engraved roller, color doctor, the pressure cylinder to back up the cloth while it is printed, and a back-grey, which is fabric to absorb any excess paste which goes through the fabric being printed. Different colors are printed with additional rollers.

Screen Printing

There are two types of screen printing. Rotary screen printing is a continuous process with the screening material stretched on a circular frame within a cylinder. Flat bed screen printing is a slower process with the screen tacked onto a flat rectangular frame.

Rotary screen printing is almost as fast as roller printing but not as expensive because the added cost of engraved rollers is not required. However, the screens cannot be used for as high volume printing as the rollers.


Dye or Pigment and Containers
Resin Binders, Thickeners, and Other Additives
Solvents
Water
Mixing
Dust
Containers with Residual Dye and Pigment
Color Paste
Fabric
Printing
Cleaning Wastes (From Equipment and Paste Containers)
Excess Paste
Recycling
To Mixing
Paste Not Recycled
Thermosol
Heat or Steam Set
Volatile Wastes
Pigment Printing
Heat Curing
Volatile Wastes
Wet Printing
Steaming
Volatile Wastes
Washing (Scouring)
Liquid Wastes
Drying
Volatile Wastes
Printed Fabric
Other Finishing
Misc. Wastes (Cloth)

Source: MRI

Figure 11-1. Typical printing process.

The process consists of covering portions of a porous screen, most commonly nickel, with a resistant material. The printing paste is then forced through the material onto the cloth while the resistant material blocks the printing paste from being printed. In this way the screen is similar to a simple stencil. A separate screen is required for each color in the design.

Flat bed screen printing is similar to rotary screen printing except the silk or synthetic cloth screen is stretched across a rectangular frame. The process may be manual, semiautomatic, or automatic. In the manual process the design is printed by forcing the paste through the screen with a squeegee. The pattern is then repeated by moving the squeegee along the fabric. The semiautomatic process differs from the manual process in that the fabric is automatically moved and positioned while the screen is kept in place but the paste is still applied manually. The automatic process does the positioning and the application automatically, but the process is virtually the same as the manual process. Although flat bed screen printing is relatively slow, the low equipment expenses make it quite economical for small shops.

Transfer Printing

Transfer printing is a dry printing technique which can refer to one of two commercially viable processes. One process is known as Thermachrome, the other as dry heat transfer (sublimation). The dye in the dry heat transfer method must vaporize rapidly at temperatures less than 150° to 220°C to avoid fabric damage. The dye must not sublime too readily, however, and must have good light and wash fastness. Disperse and basic dyes have found application in this area.

The fabric which is printed is usually a satin or glazed surface type weighing 50 to 60 g/m^2. It must have a uniform fiber structure and must not be excessively absorbent. Dyes are first dispersed in solutions of binding and thickening agents which have no affinity for the dye. Printing is typically done by conventional paper-printing methods.

Fabrics in garment or piece form printed at temperatures of 185° to 210°C and dwell times 20 to 30 sec include cellulose di- and tri-acetate; acrylics; Nylon 6 and 6/6; polyester; polyester/cotton; polyester/wool; and polyester elastane.

Thick masses of garments or fabrics can be uniformly heated and dyed by use of a press employing radio-frequency heating.

No subsequent treatment is required following printing.

Pigment Printing

The steps for pigment printing are printing of the fabric with a pigment paste and then heat curing the coloring paste. Essential constituents of the paste are the pigment and a binder to bind the pigment to the fabric. These, and other chemicals needed to give good working properties to the paste, are added to an oil-in-water or water-in-oil emulsion. One typical formulation for an oil-in-water paste contains 15% pigment (Hochberg, 1979); however, one printer stated that an average pigment concentration might be about 6% (Glick, 1979). The pigment described for these formulas is commercially available with only a 7 to 10% actual colorant concentration; therefore, the concentration of colorant in the paste would be about 0.42 to 1.5% by weight. This paste is applied to the fabric with a weight ratio of about 1:1 (RTI, 1979). The fabric is then heat cured. The only washing of the fabric is done to check the curing of the binder. If properly cured, no pigment loss should occur.

ESTIMATED PIGMENT CONSUMPTION

Pigments produced from benzidine congeners used in textile printing include: Oranges 16 and 34; Yellows 13, 14, and 83; and Blue 25. Print color is applied to specific areas of the cloth to achieve a planned design; this is often referred to as localized dyeing.

Pigments do not react chemically with the fiber to which they are being applied. Instead, a binder acts as an interface, linking the molecules of the fabric to the dye molecule. Pigment systems are easier to apply and lower in cost than dye systems (Patton, 1973).

The volume of pigments estimated to be consumed in textile printing is listed in Table 11-2. The quantities shown in this table were derived from data presented in Tables 7-3 and 7-7.

TABLE 11-2. ESTIMATED DIARYLIDE PIGMENT CONSUMPTION IN TEXTILE PRINTING

Pigment	Quantity (1,000 lb)			
	1975	1976	1977	1978
Orange 16	75	95	88	93
Orange 34	99	186	88	91
Yellow 13	36	60	56	78
Yellow 14	555	900	974	941
Yellow 83	190-220	257-287	276-336	332-392
Blue 25	163-173	147-158	139-149	130-139
Total	1,118-1,158	1,645-1,686	1,621-1,691	1,665-1,734

PIGMENT LOSSES

Roller printing pigment losses occur when the paste ink is left on the equipment before it is cleaned and by paste ink loss from the back-grey when it is washed and dried for further use. Estimates of these losses could not be obtained from industry sources because of the lack of uniformity on the number of rollers, engraving depths, and cleaning procedures. The losses are mainly solid wastes, such as paste left in the color pan, but small amounts of liquid waste result from the final equipment cleaning.

Pigment losses that occur in rotary screen printing are a result of the cleaning of the screens and other equipment. Flat bed screen printing results in pigment and dye losses during the cleaning of the equipment and paste containers. Pigment losses in transfer printing should occur only in the printing stage of the paper.

For all pigment printing processes, liquid wastes from the cleaning of the equipment were estimated to be 1 to 2% of the total amount of pigment consumed in textile printing. This range is based on information from industry sources.

For printing from a paste ink, minor miscellaneous losses will occur; the most important of these are losses from the mixing of the paste and the disposal of excess pigment. In the mixing of the dry pigments prior to paste formation, very small quantities of dye are estimated to be lost as dust particles. It is estimated that the percentage of pigment lost as dust through mixing is close to the percentage of dye dust particles (see Table 4-4).

For printing a specified amount of fabric, the printer can only estimate the amount of pigment paste required; however, the printer usually compounds an excess quantity of paste to ensure that all of the fabric can be printed. One company estimated that an average of about 10% excess pigment paste is made for each lot of fabric (Glick, 1979). Other industry sources state that excess paste loss could reach 20% for each lot. Although much of the excess paste can be incorporated into black pastes and the shading of other colors, a quantity of residual paste is discarded as solid waste. It is estimated that less than 50% of the excess paste can be recycled.

Although much of the printing is done in the same textile plants as dyeing and the colorants are packaged in a similar manner, pigment pastes are very viscous and losses from residual pigment paste remaining in their shipping or other containers are much higher than the dye losses. It is estimated that 0.5 to 2% of the pigment pastes are lost in container wastes.

Loss of dye and pigment also occurs from the final finishing of the fabric. One report stated that for the typical woven fabric dyeing and finishing processes, 1.0% of the fabric is lost in finishing after the dyeing and finishing have taken place. For the typical knit fabric dyeing and finishing process, 0.7% of the fabric is lost in finishing (Versar, 1976). It is assumed that this loss applies to the pigment and dye as well as to the cloth. This solid waste is either sold as rags, recycled and reprocessed for other end uses, or landfilled.

A summary of the sources of pigment loss and the estimated magnitude of these losses for textile printing processes is presented in Table 11-3.

TABLE 11-3. ESTIMATED DYE AND PIGMENT LOSSES IN THE TEXTILE PRINTING PROCESS

Source of loss	% Loss
Dust from mixing	0.05-0.10
Cleaning wastes from rollers, screens, squeegees, accessory equipment	1-2
Excess paste (not recycled)	5-20
Residual pigment paste in shipping containers	0.5-2
Volatile wastes from heat curing (pigment printing)	~ 0
Colorant in waste cloth from other finishing steps	0.7-1.0

The estimated pigment losses resulting from the textile printing processes are presented in Table 11-4.

TABLE 11-4. ESTIMATED DIARYLIDE PIGMENT LOSS IN TEXTILE PRINTING

Source of loss	Quantity (1,000 lb)			
	1975	1976	1977	1978
Total pigment consumed[a]	1,118-1,158	1,645-1,686	1,621-1,691	1,665-1,734
Pigment loss[b]				
Residual in shipping container (0.5-2.0%)	6-23	8-34	8-34	8-35
Mixing (0.05-0.1%)	1	1-2	1-2	1-2
Cleaning wastes (1.0-2.0%)	11-23	16-34	16-34	17-35
Excess paste (5-20%) (not recycled)	56-232	82-337	81-338	83-347
Waste cloth from finishing steps (0.7-1.0%)	8-12	12-17	11-17	12-17
Total	82-291	119-424	117-425	121-436
Total pigment in finished cloth	827-1,076	1,221-1,567	1,196-1,574	1,229-1,613

a/ Data from Table 11-2.

b/ Data from Table 11-3.

SECTION 12

MISCELLANEOUS USES

This section presents a brief discussion of a number of miscellaneous uses of benzidine, 3,3'-dimethylbenzidine, 3,3'-dimethoxybenzidine, and 3,3'-dichlorobenzidine and the dyes and pigments derived from these compounds. The areas of interest generally focus on those uses which were outside the scope of the major segments presented earlier in the report. In some instances, the areas represent a very small percentage use of certain materials while for others they may represent the sole use.

LABORATORY AND TEST APPLICATIONS

Benzidine was employed for many years in analytical and medical research laboratories for occult blood determinations, metal ion detection, chlorinated organic pesticide detection, and other analytical procedures. The advent of replacements in occult blood tests such as phenophthalein, tetramethylbenzidine, 3,3'-dimethylbenzidine, and others resulted in a gradual cessation of benzidine consumption approximately 3 to 4 years ago. The data concerning the potential health effects of benzidine were probably a major factor in the cessation of its usage. The use of benzidine as an analytical reagent for metal ions and chlorinated organic pesticides also has decreased severely; it would be currently employed only in very rare circumstances. One chemical supplier estimated that less than 1,000 lb of benzidine is currently sold for testing or other similar applications.

According to the report by Powell et al. (1979), approximately 5% (~ 10,000 lb) of the domestic usage of this compound is for various laboratory procedures such as occult blood testing or chlorine detection.

The Ames Company produces an occult blood test kit, Hematest®, that uses 3,3'-dimethylbenzidine in a tablet form. This product is sold over the counter in drugstores and similar businesses that sell medical supplies to the general public. The Ames Company declined to estimate the total consumption of the dimethylbenzidine to produce the kits or the total sales of these test kits. The company source estimated that only 1 to 2% of these kits would be used in crime laboratories, hospital laboratories, or medical research facilities.

Although no data are available regarding total consumption of the dimethylbenzidine for the various test procedures, it can be estimated that production of this material as a pellet would generally result in formulation losses of 5% or less, probably as solid waste. This estimate would include the losses resulting from blending of the dry ingredients and the pressing of the pellets. Since the pellets are dispersed into a liquid, it would appear that the vast majority of this material consumed for testing purposes would be discharged to wastewater.

HOME USE DYES

These dyes are sold in powder and liquid forms in supermarkets, drugstores, variety stores, fabric stores, and other consumer outlets. Powders are sold in packets ranging in weight from 0.5 to 2.125 oz with the commercial dye content ranging from 1% (light colors) to 45% (dark colors). Dark colored dyes dominate the market. Powdered dye packets are usually formulated to dye 1 lb of fabric. The liquid forms are sold in 8-oz containers and are formulated to dye 2 lb of fabric. Liquid dyes are much less popular than the solid dye products.

The major manufacturers of home use dyes are RIT Dyes (Best Foods Division, CPC International), Tintex (Division of Kuomark, Inc.), and Putnam (Dick Blick Materials, Inc.). An industry source estimated that RIT controls approximately 90% of the home use dye market.

Formulation

All three current manufacturers stated that benzidine based dyes are no longer used in the formulations of home use dyes. Putnam and RIT ceased using benzidine based dyes in 1976; RIT had exhausted all stock containing benzidine based dyes by 1977. Tintex ceased formulation with these dyes in late 1977 and had exhausted all stock by October 1978. All three producers stated that they currently formulate their products using dyes based on 3,3'-dimethylbenzidine and 3,3'-dimethoxybenzidine in conjunction with other dyes.

NIOSH (1980b), however, found that 13 of 15 samples of retail dyes bought in the fall of 1978 in New York City contained benzidine-based dye. The dye samples were chemically reduced and analyzed for benzidine, 3,3-dimethylbenzidine, 3,3'-dimethoxybenzidine, and analine. The relative percent benzidine (percent of the total reduced components) averaged 57% (range 1 to 100%).

Consumption

Dyes based on 3,3'-dimethylbenzidine which are currently employed in home use products are Direct Blue 14, Direct Orange 6, Direct Red 2, and Direct Red 39. Dyes that are based on 3,3'-dimethoxybenzidine are Direct Blue 1, Direct Blue 218, and Direct Blue 80 (Battelle, 1979). Between 60 and 70% of all colorant packets in the home use market contain dyes based on 3,3'-dimethylbenzidine or 3,3'dimethoxybenzidine.

All three formulators were contacted but could provide no information on the total consumption of the dyes of interest during the period 1975 through 1978. Data in the Battelle report show that for 1978, an estimated

400,000 lb of all dye types were consumed to produce home use dye packets. Of this quantity, an estimated 33% (~ 130,000 lb) were dyes based on dimethyl- or dimethoxybenzidine. The total number of dye packets produced in 1978 was 25 to 30 million. Approximately 50 million packets of dye were produced in 1975 (Jenkins, 1978).

No data were available for the total number of packets produced in 1976 or 1977; prorated production figures for these 2 years estimate the number of packets in 1976 at 40 to 45 million and at 30 to 40 million in 1977.

Using 1978 data for dimethyl- or dimethoxybenzidine-based dye consumption (130,000 lb) and the average total number of packets produced (27.5 million), an average quantity of dye per packet can be obtained. This average quantity per packet was used to estimate quantities for 1975 (230 to 255,000 lb), 1976 (190 to 215,000 lb), and 1977 (140 to 195,000 lb). No information could be obtained from industry sources which would permit any further evaluation of these quantities with respect to the percentage based on dimethylbenzidine or dimethoxybenzidine.

Estimated Losses

For the purposes of these estimations, it is assumed that all dye is formulated into dry packets. This assumption is based on the knowledge that liquid dye products represent a small percentage of the market and that formulating losses for the liquid would likely be equal or less than losses for a dry packet.

No data were available from home dye manufacturers concerning formulation losses. In most of the industries discussed earlier in this report, the formulation of dyes into dry mixes resulted in average losses of approximately 2 to 3% as residual dye in the shipping containers, handling losses, dust losses from mixing, and other losses. This loss range, then, will be assumed for these products. For the dyeing process in the home, an exhaustion (uptake of dye on fabric) of about 25 to 40% was assumed. The remaining 60 to 75% of the dye was discharged to the sewer. These estimated losses are summarized in Table 12-1.

TABLE 12-1. ESTIMATED LOSSES FROM HOME DYES

Loss source	Quantity (1,000 lb)[a/]			
	1975	1976	1977	1978
Total dye used	115-128	95-108	70-98	60-65
Formulation losses (2-3%)	2-4	2-3	1-3	1-2
Wastewater loss (60-75%)	69-96	57-81	42-74	36-49
Dye on finished fabric	15-57	11-49	10-55	9-28

[a/] Based on 100% dye; for method of calculation, see Table 5-5, footnote d.

ARTS AND CRAFT DYES

The market for arts and crafts dyes is very fragmented with respect to both the supply and demand segments. Most of the dyes used in crafts are either the industrial dyes which have been specially packaged for craft use or the home-use dye (see preceding subsection). The specially packaged craft dyes are more concentrated than the home-use dyes. Potential users of the specially packaged dyes are reached by direct mail advertising, craft oriented magazines, or through specialty shops. Distributors of the dyes may employ imported, prepackaged dyes or may purchase bulk quantities. The bulk quantities may be repackaged directly for resale or used in the formulations of dye mixture for resale.

Fifteen consumer retail dyes were bought at arts and crafts shops in New York City and analyzed for BEN, DMB, and DMOB. All 15 samples were shades of blue, black, or brown (NIOSH, 1980b). It is unknown whether these are the only BEN, DMB, or DMOB dyes available or only the ones selected for analysis.

Arts and crafts dyes are used for a multitude of coloring applications with textiles, wood, paper, glass, metal, and other materials. The degree of dye absorpton into the material ranges from very high (e.g., textiles) to very low (e.g., glass, metal).

The annual consumption of dyes based on dimethyl- or dimethoxybenzidine in this area is very small. Estimates of total annual consumption range from 10,000 to 20,000 lb of commercial dye and consumption has remained in this range since 1975 (Sheldrick, 1979). It is estimated that approximately 20% of the total quantity is discarded as solid or liquid waste during formulation and consumer use of these products and that about 80% of the total quantity is contained in the finished product. Of the 20% which is discarded, 75% is estimated to be solid waste and 25% wastewater. Thus, for each year since 1975, approximately 4,000 to 8,000 lb of 100% dye were contained in the finished product and 1,000 to 2,000 lb of 100% dye were discarded. Of these estimated losses, 750 to 1,500 lb are estimated to be solid waste and 250 to 500 lb discharged to the sewer.

MARKING INSTRUMENTS

Pigments derived from dimethylbenzidine (Orange 15) and dimethoxybenzidine (Orange 16) were used in the production of children's crayons, lumber marking crayons, china marking pencils, paint sticks, carpenter markers, and other similar products. Orange 15 is no longer produced in the United States, and in 1978 import quantities were very small.

Formulation

Most of these products are formulated in basically the same manner. For children's crayons, a mixture of paraffin and stearic acid is melted in a steam kettle, the colorants added, and the liquid wax mixture poured into molds. Circulating cold water chills the molds and solidifies the wax mixture. The crayons are ejected, trimmed, and paper wrapped.

Industrial crayons are produced in a slightly different manner. The most popular type of industrial crayons is composed of kaolin, color pigment, and either natural or synthetic gum as the binder. All ingredients are mixed with water to form a mass with dough-like consistency. This mass is extruded, dried, and then impregnated with wax. Other methods of production include dry pressing with a powdered wax mixture and the use of melted wax mixtures as described for children's crayons.

Consumption

Orange 15 and Orange 16 are the only two pigments of interest consumed in this area. Estimated total quantities of the two pigments were derived from Tables 7-3 and 7-7. The estimated total annual consumption is as follows: 1975 (93,000 to 98,000 lb), 1976 (107,000 to 112,000 lb), 1977 (96,000 to 101,000 lb), and 1978 (66,000 lb).

Estimated Losses

Estimated losses during the production of the hot wax mixture should be very small. The only anticipated losses result from the handling of the dry pigment during weighing, and very small losses due to residual pigment in containers. In previous sections of this report, these losses have been estimated to be less than 0.5%. The only other production losses would be due to trimmings from the cast or extruded crayons. It is estimated that these losses would not be greater than 2.5 to 3.5%. All losses from the production process would likely be treated as solid waste. The estimated quantities of loss are presented in Table 12-2.

TABLE 12-2. ESTIMATED LOSSES FROM CRAYON PRODUCTION

	Quantity (1,000 lb)[a]			
Loss source	1975	1976	1977	1978
Total pigment used	93-98	107-112	96-101	66
Pigment loss				
Mixing and handling (0.5%)	~ 0.5	~ 0.5	~ 0.5	~ 0.3
Trimming (2.5-3.5%)	2.5-3.3	2.7-3.9	2.4-3.5	2.3
Total	3-4	3-4	3-4	~ 3
Pigment in finished crayon	89-95	103-109	92-98	63

a Derived from Tables 7-3 and 7-7.

OTHER BAB DYE USES

In addition to the information presented in this report on uses of BAB dyes, quantities are also used in other areas for which little or no information could be developed. The lack of data is a result of either significant uses in specific areas considered to be proprietary or very small usage in a multitude of areas.

Information from DETO (DETO, 1980) indicates that approximately 340,000 lb of dye based on 3,3'-dimethylbenzidine has been consumed annually since at least 1975 for miscellaneous uses in the coloration of lubricants, gasoline, and other fuels. The specific dye or dyes are manufactured by one company and all information concerning these products is proprietary. No further information could be derived for these products.

It is recognized that quantities of BAB dyes are sold through formulators or repackagers (companies who purchase in bulk and repackage in smaller quantities) for a variety of uses. Little information is known concerning the total quantity of dyes employed in these uses, the specific dyes being employed, or the uses for the dyes. In general, the quantities employed are small and the uses are extremely varied. However, the cumulative quantity of a specific type of BAB dye (e.g., 3,3'-dimethoxybenzidine-based) could reach 4 to 5% of the total quantity consumed in 1 year. Due to the diversity of the uses and the quantities of dye involved with each use, no information was developed for these areas.

SECTION 13

PRELIMINARY MATERIALS BALANCE

This section contains a preliminary overall materials balance for BAB dyes and for selected pigments produced in the United States from 1975 to 1978.

The overall balance has been divided into two parts, BAB dyes and pigments. In each balance the size of the range reported for each value is indicative of the uncertainty associated with the specific estimate. Detailed descriptions of the technique used to generate individual estimates as well as the uncertainties involved are contained in the appropriate sections of this report.

BAB DYES

Table 13-1 provides estimates of the losses of BAB dyes during the dye production processes. These losses result from processing and filtration losses during dye production, and product losses during drying, blending, and final packaging.

Table 13-2 summarizes a materials balance for the BAB dyes in specific use areas. Estimates are provided for the quantitities of dye production resulting in the final products (commercial products or end uses), solid waste, liquid waste, and losses to the air. All data are expressed in thousands of pounds of dye. The data are presented in terms of ranges rather than single values. This results because in the calculations, ranges were employed for the percentage use in specific areas and for the magnitude of the various sources of BAB dye loss during manufacture and consumption. As a result, the data in Table 13-2 represent minimum and maximum levels rather than average levels, which would have been the result if single values had been employed.

As stated in Section 12, all uses of BAB dyes have not been characterized in this study and are not represented in Table 13-2. These uses, although very small individually, can cumulatively account for up to 4 to 5% of the total annual use of a type of BAB dye (e.g., benzidine-based). Thus, the material balance accounts for the significant major uses of BAB dyes but does not present a complete accounting for all losses resulting from all possible uses.

TABLE 13-1. BAB DYE LOSSES FROM PRODUCTION PROCESSES

	Active Dye Loss (1,000 lb)											
	1975			1976			1977			1978		
Distribution	BEN[b]	DMB[c]	DMOB[d]	BEN	DMB	DMOB	BEN	DMB	DMOB	BEN	DMB	DMOB
Processing losses (0.21-0.95%)[e]	5-26	< 1-4	1-8	7-40	< 1-4	2-10	5-26	< 1-4	1-7	2-10	< 1-5	2-12
Filtration losses (1-3%)	23-84	4-13	6-24	35-130	4-14	9-32	25-82	4-14	6-22	9-31	4-16	10-38
Drying, grinding, standardization, and packaging losses (1-5%)	23-140	4-22	6-40	35-210	4-23	9-53	25-140	4-23	6-36	9-52	4-26	10-63

---

[a] These data, which correspond to those given in Table 3-4, are on active dye basis. An overall product yield of 85% (BAMB raw material base) has been assumed.

[b] BEN = benzidine-based dyes.

[c] DMB = dimethylbenzidine-based dyes.

[d] DMOB = dimethoxybenzidine-based dyes.

[e] For the methods of calculation used in this table, see Appendix B,1.

TABLE 13-2. ESTIMATED MATERIALS BALANCE FOR BAB DYES BY USE AREA

	Quantities (1,000 lb)[a]			
	Textile	Leather	Paper	Home dyes[b]
Final Product				
1975	642-2,170	357-817	611-1,081	19-65
1976	592-2,754	455-1,114	843-1,616	15-54
1977	601-2,270	522-1,088	787-1,355	14-63
1978	508-1,794	585-1,304	501-920	13-36
Losses				
Solid waste:				
1975	18-38	53-174	39-168	3-6
1976	20-48	69-236	55-250	3-5
1977	18-39	75-232	50-210	2-5
1978	15-32	86-277	32-142	2-4
Liquid waste:				
1975	112-920	0.1-0.2	0.1-0.2	69-96
1976	126-1,160	0.1-0.2	0.1-0.3	57-81
1977	112-960	0.1-0.2	0.1-0.2	42-74
1978	91-760	0.1-0.3	0.1	36-49
Air losses:				
1975	neg.[c]	0.1-0.2	0.1-0.2	neg.
1976	neg.	0.1-0.2	0.1-0.3	neg.
1977	neg.	0.1-0.2	0.1-0.2	neg.
1978	neg.	0.1-0.3	0.1	neg.

Summary

	1975	1976	1977	1978
Total dye in final products	1,629-4,133	1,905-5,538	1,924-4,776	1,607-4,054
Losses				
Solid	113-386	147-539	145-486	135-455
Liquid	181-1,016	183-1,241	154-1,034	127-809
Air	neg.	neg.	neg.	neg.
Total Losses	294-1,402	330-1,780	299-1,520	262-1,264

[a] Quantities are in terms of 100% dye, not standardized commercial dye.

[b] Includes arts and crafts uses.

[c] Negligible losses.

PIGMENTS

Table 13-3 presents an estimate of the losses of 3,3'-dichlorobenzidine (DCB), 3,3'-dimethoxybenzidine (DMOB), and 3,3'-dimethylbenzidine (DMB) occurring during the manufacture of these three materials and during reactions consuming these materials to form the desired pigments. For example, in 1978 it is estimated that 7,445,000 to 7,531,000 lb of DCB were produced. Of this total quantity, 78,000 to 196,000 lb were lost in wastewater from various stages of the manufacturing process and 38,000 to 77,000 lb were lost in wastewater from various stages of the pigment production process. All wastewater from both the manufacturing process and pigment production process is treated prior to disposal. Thus, 7,258,000 to 7,329,000 lb were estimated to be used to produce all DCB-based pigments in 1978.

Losses of pigment occur due to handling and transfer during the process of transforming the pigment into a packaged, finished pigment ready for shipment to the user. These estimated losses of pigment are shown in Table 13-4. The losses presented in Table 13-4 are based on the maximum estimated annual pigment production levels presented earlier in Section 7.

The estimated materials balance for pigments based on DCB, DMOB, and DMB in specific use areas is shown in Table 13-5. As with the BAB dyes, the data are presented in terms of ranges rather than single values. In the calculations, ranges were employed for the percentage use in specific areas and for the magnitude of the various sources of pigment loss during manufacture and consumption. As a result, the data in Table 13-5 represent minimum and maximum levels rather than average levels, which would have been the result if single values had been employed.

OVERALL PERSPECTIVE

This subsection presents a brief discussion of the availability and reliability of data on the production and use of BAB dyes and on the data for pigments. Needs for additional information in each of these areas are defined.

Dye and Pigment Production

In an overall perspective, more data are available and the sources of loss are better defined for this area than any other general area considered in this material balance. The production processes are fairly well defined as are the relevant sources of loss in the BAB dye production process. However, additional detailed information is required for pigment production since only a rather generalized procedure is described.

Pigment production quantities and the extent of pigment usage by the various industries are considerably better defined than the corresponding information for dyes. The percent utilization of a given pigment or BAB dye by various industries will, of necessity, be a matter of conjecture since estimates obtained from various manufacturers will differ.

TABLE 13-3. ESTIMATED LOSSES OF RAW MATERIAL DURING MANUFACTURE AND PIGMENT PRODUCTION

Base	Losses (x 10^3 lb) Manufacture	Losses (x 10^3 lb) Pigment prod.[a]	Consumed in pigments[b] (x 10^3 lb)
DCB[c]			
1975	40-102	20-40	3,762-3,799
1976	56-140	27-54	5,180-5,215
1977	62-155	30-61	5,742-5,811
1978	78-196	38-77	7,258-7,329
DMOB[d]			
1975	2-6	1-2	215-226
1976	2-7	1-3	250-261
1977	2-7	1-3	233-244
1978	2-7	1-3	240-251
DMB[e]			
1975	0.2-0.5	0.1-0.2	14-16
1976	0.2-0.5	0.1-0.2	14-16
1977	0.2-0.4	0.1-0.2	13-14

[a] Excludes optional processes.

[b] Excludes the ~20 ppm of base dihydrochloride salt remaining on pigment.

[c] DCB = 3,3'-dichlorobenzidine.

[d] DMOB = 3,3'-dimethoxybenzidine.

[e] DMB = 3,3'-dimethylbenzidine.

TABLE 13-4. ESTIMATED PIGMENT LOSS IN PRODUCTION PROCESS

	Quantity (1,000 lb)			
	1975	1976	1977	1978
Total pigment production				
DCB[a]	9,875-10,056	13,565-13,815	15,147-15,417	19,050-19,404
DMOB[b]	623-636	707-722	661-674	677-691
DMB[c]	~46	~46	~46	-
Estimated pigment losses				
DCB	91-274	126-380	137-410	177-537
DMOB	6-19	7-21	6-20	6-20
DMB	0.5-1	0.5-1	0.4-1	-
Total pigment for sale or captive use				
DCB	9,666-9,781	13,324-13,434	14,787-15,007	18,641-18,866
DMOB	587-617	670-700	624-654	640-670
DMB	40-45	40-45	35-40	-

[a] DCB = 3,3'-dichlorobenzidine.
[b] DMOB = 3,3'-dimethoxybenzidine.
[c] DMB = 3,3'-dimethylbenzidine

TABLE 13-5. ESTIMATED MATERIALS BALANCE FOR 3,3'-DICHLOROBENZIDINE, 3,3'-DIMETHYLBENZIDINE AND 3,3'-DIMETHOXYBENZIDINE BASED PIGMENTS IN USE AREAS

	Quantities (1,000 lb)					
	Printing ink	Textile printing	Plastics	Coatings	Rubber	Misc. Uses[a]
Final product						
1975	6,033-6,662	827-1,076	689-843	481-498	46-47	89-95
1976	8,189-9,026	1,221-1,567	954-1,139	690-709	69-71	103-109
1977	8,997-9,963	1,196-1,574	1,023-1,251	784-811	73-75	92-98
1978	11,698-12,921	1,229-1,613	1,122-1,366	949-980	71-73	63
Losses						
Solid waste:						
1975	1,085-1,672	71-268	42-135	7-11	~1-2	3-4
1976	1,472-2,266	103-390	58-183	10-16	~2-4	3-4
1977	1,619-2,499	101-391	62-200	12-18	~2-4	3-4
1978	2,104-3,243	104-401	68-218	14-21	~2-4	~3
Liquid waste:						
1975	117-118	11-23	Neg.[b]	2-3	Neg.	Neg.
1976	159-160	16-34	Neg.	3-4	Neg.	Neg.
1977	175-176	16-34	Neg.	~4	Neg.	Neg.
1978	228-229	17-35	Neg.	4-5	Neg.	Neg.

SUMMARY

	1975	1976	1977	1978
Total production range including imports	10,418-10,568	14,310-14,455	15,510-15,765	19,316-19,571
Total pigment in final products	8,165-9,221	11,226-12,621	12,165-13,772	15,132-17,016
Losses				
Solid	1,209-2,092	1,648-2,863	1,799-3,116	2,295-3,890
Liquid	130-144	178-198	195-214	249-269
Air	Neg.	Neg.	Neg.	Neg.
Total	1,339-2,236	1,826-3,061	1,994-3,330	2,544-4,159

---

[a] Crayons and other marking instruments.

[b] Negligible.

The information obtained for this report for the dye production process was more detailed than for pigment production so that fewer assumptions and estimations were necessary. On balance, these data are better defined than for the pigment manufacturing process. Analytical data for the quantities of 3,3'-dimethoxybenzidine and 3,3'-dimethylbenzidine currently being discharged in wastewater would be of interest to better define the magnitude of these losses during the manufacturing process.

One of the major areas of estimation in this report is the production and import of the BAB dyes of interest. Since very few data were available, gross estimates of the U.S. production and import quantities of the specific BAB dyes were necessitated. Because these data are one of the keystones for estimating potential losses from user industries, more detailed information is critically required in this area.

BAB Dye Consumption

With the BAB dye industry, it is extremely difficult to evaluate with any degree of accuracy the consumption of specific BAB dyes by a particular user industry. In many respects, this inability arises from the wide diversity observed among the various manufacturers in the textile, leather, and paper industry. Another contributing factor, especially in the leather industry, is the use of prepackaged dye formulations which are prepared by small speciality businesses for the particular tannery.

In the report, the estimated losses resulting from BAB dye consumption in the leather, textile, and paper industries have the largest degree of uncertainty of all the inputs to the material balance.

Losses resulting from the various processes employed within a specific industry (e.g., textiles, leather, etc.) are extremely difficult to ascertain with any degree of accuracy primarily because of the multitude of variations employed by the individual companies. Because of this, generalized processes were employed to estimate overall losses that might be anticipated.

One of the major deficiencies in the available data is the lack of information concerning the levels of BAB dye being discharged by these user industries. If such data were available, the assumptions employed to obtain the estimated data could be reevaluated and the degree of accuracy refined. Sampling studies have been performed at sites in a number of different industries but very few data are available concerning specific effluent levels. At the various sampling sites, the parent compound is the species under investigation, not the discharged BAB dye. Reliable data are necessary for the quantities of BAB dyes being discharged from the various user facilities before an accurate evaluation of the processes occurring within an industry can be completed.

Pigment Consumption

On the surface, it appears that the major pigment users have a more refined estimation of the sources of pigment loss and the magnitude of each loss. The printing ink industry totally dominates the user market for pigments; in 1978 they accounted for the use of approximately 74% of the total quantity of all pigments of interest to this study. Most printing ink companies purchase either dry toner or flushed color pigments and develop the printing ink. Because of this practice and the methodology of ink production, this industry appears to be able to define pigment losses within a much more narrow range than those industries associated with BAB dye consumption. The paint and coatings industry appears to be very similar to the printing ink in the ability to define the sources and magnitude of pigment loss. Other industries consuming pigments were not able to define the losses to the same degree of accuracy. For the plastics industry, the very diverse nature of that industry probably contributes to a large degree to the overall inability to be more definitive. In addition, some of the mechanical processes used lead to wide variations in the magnitude of the losses.

As with the area of BAB dye consumption, the major deficiency in the data available on pigment loss lies with the lack of data on the quantity of pigments discharged from the user facilities. To a large degree the statements made previously with respect to data needs for a more definitive evaluation of BAB dye consumption are equally valid for the area of pigment consumption. Since the major consumers of pigments appear to have more refined estimates of pigment loss, the need for quantitative data on pigment discharges may not be as critical as for the BAB dye consuming industries.

REFERENCES

Anon. 1978a. American Ink Maker. May 1978. p. 24.

Anon. 1978b. Organic Pigments: Sales, Production, Imports, Exports (using 1977 Census Data). American Ink Maker. December 1978. p. 19.

Anon. 1979. Cradle to Grave Waste Disposal. American Ink Maker. January 1979. p. 15.

Asher, D. 1979. DeSoto Coatings, Chicago, Illinois. Personal communication to H. Gadberry. July 24.

Barnett, S. 1979. General Printing Ink Company, Kansas City, Missouri. Personal communication to H. Gadberry. June 14.

Barrett, W. J. 1973. Waterborne Wastes of the Paint and Inorganic Pigment Industries. Southern Research Institute. EPA 670/2-74-030. Environmental Protection Agency, Washington, D.C. July.

Battelle. 1979. Final Report on Product/Industry Profile: Dyes Based on Benzidine Congeners. CPSC-C-78-0091, Task 5. U.S. Consumer Product Safety Commission. Washington, D.C. April 16.

Bleaskiewcz, A. 1979. Uniroyal Chemical, Naugatuck, Connecticut. Telephone communication to B. Thompson. July 31.

Bochner, B. 1979. Personal communication of Dr. Barry Bochner, Atlantic Chemical Company to Dr. Thomas W. Lapp, Midwest Research Institute. July 24.

Boeniger, M. 1979. Technical Report on the Carcinogenicity and Metabolism of Azo Dyes, Especially Those Derived from Benzidine. National Institute for Occupational Safety and Health, Cincinnati, Ohio.

Bognar, R. 1979. American Paper Institute, New York, New York. Telephone communication to F. Hopkins. July 19.

Borum, R. 1979. Printing Industries of America, Arlington, Virginia. Telephone communication to H. Gadberry. June 27.

Bratchler, R. 1979. McKessen Chemicals Corporation, Kansas City, Missouri. Personal communication to H. Gadberry, June 20.

Bruhns, R. 1971. The Paint Industry vs. Water Pollution. Paint and Varnish Production. March 1971.

Bruno, M. H. 1978. Printing in the USA. American Ink Maker. February 1978. p. 19.

Bureau of the Census. 1976a. Wool Broadwoven Goods: 1975 Current Industrial Reports. U.S. Department of Commerce, Washington, D.C. September 1976.

Bureau of the Census. 1976b. Broadwoven Fabric Finished: 1975. Current Industrial Reports. MA-22S(75)-1. U.S. Department of Commerce, Washington, D.C. August 1976.

Bureau of Census, 1977a. Finished Broadwoven Fabric Production: 1976. Current Industrial Reports. MA-22S(76)-1. U.S. Department of Commerce, Washington, D.C. June 1977.

Bureau of the Census. 1977b. Knit Fabric Production: Summary for 1976. Current Industrial Reports. MQ-22K(76)-5. U.S. Department of Commerce, Washington, D.C. November 1977.

Bureau of the Census. 1977c. Wool Broadwoven Goods: 1976. Current Industrial Reports. MA-22T.3(75)-5. U.S. Department of Commerce, Washington, D.C. September 1977.

Bureau of the Census. 1978a. Finished Broadwoven Fabric Production: 1977. Current Industrial Reports. MA-22S(77)-1. U.S. Department of Commerce, Washington, D.C. August 1978.

Bureau of the Census. 1978b. Knit Fabric Production: Summary for 1977. Current Industrial Reports. MQ-22K(77)-5. U.S. Department of Commerce, Washington, D.C. November 1978.

Bureau of the Census. 1978c. Knit Fabric Production: Second Quarter 1978. Current Industrial Reports. MQ-22K(78)-2. U.S. Department of Commerce, Washington, D.C. September 1978.

Bureau of the Census. 1979a. Knit Fabric Production: Fourth Quarter 1978. Current Industrial Reports. MQ-22K(78)-4. U.S. Department of Commerce, Washington, D.C. March 1979.

Bureau of the Census. 1979b. Finished Broadwoven Fabric Production: 1978. Current Industrial Reports. MA-22S (78)-1. U.S. Department of Commerce, Washington, D.C. August 1979.

Bureau of the Census. 1979c. Broadwoven Fabrics (Gray): Summary for 1978. Current Industrial Reports. MO-22T (78)-5. U.S. Department of Commerce, Washington, D.C. December 1979.

Burns and Roe. 1979a. Effluent Limitations Guidelines for the Ink Manufacturing Industry. Environmental Protection Agency, Washington, D.C. January 1979.

Burns and Roe. 1979b. Effluent Guidelines for the Paint Manufacturing Industry. Burns and Roe, EPA Draft, January.

Byrd, R. 1979. Enmar-Wichita Division of Ameron Corporation, Wichita, Kansas. Personal communication to H. Gadberry. July 13.

Census. 1972. Census of Manufacturers, 1972. U.S. Department of Commerce, Bureau of the Census, Washington, D.C.

Census. 1977. Census of Manufacturers, 1977. U.S. Department of Commerce, Bureau of the Census, Washington, D.C.

Colour Index (3rd ed.). 1971. Published by the Society of Dyers and Colourists. Bradford, England, and the American Association of Textile Chemists and Colorists, Research Triangle Park, North Carolina.

Conrad, E. T. et al. 1976. Assessment of Industrial Hazardous Waste Practices--Leather Tanning and Finishing Industry. EPA 68-01-3261. PB 261 018. Environmental Protection Agency, Washington, D.C. 244 pp.

Continental Forest Industries, Inc. 1978. Paperboard: Types, Methods of Manufacture, How Packagers Specify. Modern Packaging Encyclopedia and Buyer's Guide, 51(2):37-43. December.

Cramsie, J. 1979. St. Regis Paper Company, West Nyack, New York. Telephone communication to F. Hopkins. July 17.

Danforth, D. W. 1970. Beating and Refining Equipment. Handbook of Pulp and Paper Technology, 2nd Edition, K. W. Britt, ed. Van Nostrand Reinhold Company, New York, New York. pp. 333-344.

DeSoto. 1974. DeSoto Coatings Corporation. DeSoto Waste Treatment System for Latex Paint Wastes. Des Plains, Illinois.

Dry Color Manufacturers Association (DCMA). 1979. Arlington (Rosslyn), Virginia. Letter to Ms. Elizabeth F. Bryan, Office of Pesticides and Toxic Substances, Environmental Protection Agency, Washington, D.C. November 13.

Dyes Environmental and Toxicology Organization (DETO). 1979. Bisazobiphenyl Dyes Currently on the U.S. Market (July 1979 correction). (unpublished).

Dyes Environmental and Toxicology Organization (DETO). 1980. Letter from Dr. Patrick A. Florio, American Hoechst Corporation, as a spokesman for the Dyes Environmental and Toxicology Organization; April 10, 1980.

Ensminger, C., and M. Culp. 1979. Enmar-Little Rock, division of Ameron Corporation, Little Rock, Arkansas. Telephone communication to H. Gadberry. July 10.

Environmental Protection Agency (EPA). 1973. Field Notes and Chemical Analyses--Survey of Paint and Ink Manufacturers in Oakland, California. National Field Investigations Center, Denver, Colorado. October.

Environmental Protection Agency (EPA). 1976. Assessment of Industrial Waste Practices: Paint and Allied Products Industry, Contract Solvent Reclaiming Operations and Factory Application of Coatings. EPA, Washington, D.C.

Environmental Protection Agency (EPA). 1977. Toxic Pollutant Effluent Standards for Aldrin/Dieldrin, Benzidine, DDT (DDD, DDE), Endrin and Toxaphene; Final Decision. Federal Register, 42(8):2587-2621.

Environmental Protection Agency (EPA). 1979a. National Pollution Discharge Elimination System; Revision of Existing Regulations. Federal Register, 44(166):34412.

Environmental Protection Agency (EPA). 1979b. Draft, Development Document for Proposed Effluent Limitations Guidelines, New Source Performance Standards, and Pretreatment Standards for the Textile Mills Point Source Category. Effluent Guidelines Division. Office of Water and Waste Management. May 1979.

Fagan, J. 1979. Vile-Goller/Fine Arts Printing, Kansas City, Missouri. Personal communication to H. Gadberry. June 29.

Festo, J. 1979. American Paper Institute, Washington, D.C. Telephone communication to F. Hopkins. June 21.

Florio, P. 1979. American Hoechst, Inc., Sommerville, New Jersey (DETO spokesman for dyes). Telephone communication to F. Hopkins. August 10.

Florio, P. 1980. American Hoechst, Inc., Sommerville, New Jersey (DETO spokesman for dyes). Personal communication to Dr. Thomas W. Lapp. April 10.

Francke, D. W., R. E. Seltzer, and D. J. Wissman. 1978. Economic Impact Analysis of Hazardous Waste Management Regulation on the Leather Tanning and Finishing Industry. EPA-530/SW-157c. PB 279 773. EPA, Washington, D.C. 124 pp.

Franklin, W. E., et al., 1979. Solid Waste Management and the Paper Industry. The Solid Waste Council of the Paper Industry. February 1979. 279 pp.

Funaroff, S. 1979. American Paper Institute, New York, New York. Telephone communication to F. Hopkins. July 25.

Gallup, J. D. 1974. Development Document for Effluent Limitations Guidelines and New Source Performance Standards for the Leather Tanning and Finishing Point Source Category. EPA 440/1-74-016-a. PG 238 648. EPA, Washington, D.C. 161 pp.

Gilbert, W. 1979. General Printing Ink Division of Sun Chemical Company, Kansas City, Missouri. Personal communication to H. Gadberry. July 19.

Glick, H. 1979. Revere Textile Printing, Sterling, Connecticut. Telephone Communication to B. Thompson. July 2.

Greer, B. 1979. Harwick Chemical Corporation, Akron, Ohio. Telephone communication to F. Hoffmeister. July 30.

Hahn, N. 1979. Cook Paint and Varnish Company, Kansas City, Missouri. Telephone communication to H. Gadberry. June 22.

Harrison, C. S. 1979. U. S. Leather Processors Link Their Fate to Decision on Export Controls on Hides. Wall Street Journal. July 31, 1979. p. 30.

Hine, W. R. 1971. Disposal of Waste Solvents. Journal of Paint Technology, 43(588):75-78. July 1971.

Hochberg, E. G. 1979. The Market for Textile Printing Chemicals. Textile Chemist and Colorist, Vol. 11, No. 5. May 1979. pp. 89-90.

International Trade Commission (ITC). 1976a. Synthetic Organic Chemicals. U.S. Production and Sales, 1975. Washington, D.C.

International Trade Commission (ITC). 1976b. Imports of Benzenoid Chemicals and Products, 1975. Washington, D.C.

International Trade Commission (ITC). 1977a. Synthetic Organic Chemicals. U.S. Production and Sales, 1976. Washington, D.C.

International Trade Commission (ITC). 1977b. Imports of Benzenoid Chemicals and Products, 1976. Washington, D.C.

International Trade Commission (ITC). 1978a. Synthetic Organic Chemicals. U.S. Production and Sales, 1977. Washington, D.C.

International Trade Commission (ITC). 1978b. Imports of Benzenoid Chemicals and Products, 1977. Washington, D.C.

International Trade Commission (ITC). 1979. Imports of Benzenoid Chemicals and Products, 1978. Washington, D.C.

Jenkins, C. L. 1978. Scientific Basis for the Proposed Regulation of Dyes Derived from the Chemical Substances Benzidine, 3,3-Dimethylbenzidine, and 3,3'-Dimethoxybenzidine. Appendix I. Petition to the Secretary of Labor. May 15, 1978. 79 pp.

Johnson, S. 1979. Cook Paint and Varnish Company, Kansas City, Missouri. Telephone communication to H. Gadberry. July 10.

Kasprzak, S. J. 1979. Dyes Environmental and Toxicology Organization, Scarsdale, New York. Letter to Ms. Elizabeth F. Bryan, Office of Pesticides and Toxic Substances, Environmental Protection Agency, Washington, D.C. November 15.

Keinath, T. M. 1976. Benzidine: Wastewater Treatment Technology. EPA-440/9-76-018, Environmental Protection Agency, Washington, D.C. 131 pp.

Kent, J. A. (ed.). 1974. Riegel's Handbook of Industrial Chemistry. (7th ed.). Van Nostrand Reinhold Company, New York. 902 pp.

Landerl, Dr. E. I. 1979. E. I. DuPont de Nemours, Wilmington, Delaware. Telephone communication to F. Hopkins. July 18.

Lips, H. A. 1970. Handbook of Pulp and Paper Technology, 2nd ed. K. W. Britt, ed. Van Nostrand Reinhold Company, New York, New York. pp. 369-376.

Lollar, R. M. 1979. Technical Director, Tanner's Council of America, Cincinnati, Ohio. Telephone communication to F. Hopkins. June 25.

Maas, W. 1972. Solid Waste Disposal and Organic Finishing. Metal Finishing. March 1972.

Maida, S. M. 1978. Review of Gravure on the Move. American Ink Maker. August 1978. P. 19.

Materozzi, A. R. 1976. U.S. Government Printing Office. In: Environmental Aspects of Chemical Use in Printing Operations. EPA-560/1-75-005. EPA, Washington, D.C. January 1976.

McGrew, H. 1979. McGrew Color Graphics, Kansas City, Missouri. Personal communication to H. Gadberry. June 5.

Mellan, C. 1979. Sherwin Williams Company, Cleveland, Ohio. Telephone communication to H. Gadberry. July 11.

Midwest Research Institute (MRI). North Star Division. 1977. Draft, Addendum to the Pretreatment Supplement on Best Available Technology Economically Achievable for the Leather Tanning and Finishing Point Source Category. EPA Contract No. 68-01-3275. EPA, Washington, D.C. 168 pp.

Midwest Research Institute (MRI). 1979a. Detection of Lead in Printing Ink Factory Atmosphere. MRI Project No. 4750-L. April 1979.

Midwest Research Institute (MRI). 1979b. Ink Residues Determined by Weight Differences at Typical Commercial Printing Establishments. July 5-19.

Midwest Research Institute (MRI). 1979c. Paint Composition Labels from 200 Packages of Cream, Yellow, Gold, and Orange Paints were Inspected to Determine the Proportion Containing Diarylide Pigments. The most frequent usage was found in yellow enamel sprays and orange primers.

Miller, E. 1979. Glidden Division of SCM, Inc., Cleveland, Ohio. Telephone communication to H. Gadberry. June 26.

Modern Plastics. 1976. In Chemicals and Additives, Regulation Casts a Shadow: Colorants. Modern Plastics, September 1976. pp. 46-48.

Modern Plastics. 1977a. Plastics Sales Data, 1976 vs. 1975: Back Over the 13,000,000-ton Mark. Modern Plastics. January 1977. pp. 49-52.

Modern Plastics. 1977b. Living with the New Regulations: Colorants. Modern Plastics, September 1977. pp. 52-55.

Modern Plastics. 1978a. Market 1978. U.S. Plastics Sales Data; 1977 vs. 1976. Modern Plastics, January 1978. pp. 49-55.

Modern Plastics. 1978b. Opening the Doors to New Markets: Colorants. Modern Plastics, September 1978. pp. 54-57.

Modern Plastics. 1979. Materials 1979. Modern Plastics, January 1979. pp. 45-69.

Modern Plastics Encyclopedia. 1978. Modern Plastics Encyclopedia 1978-1979. McGraw-Hill, Inc.

Mullen, G. 1979. Devilbliss Corporation, Toledo, Ohio. Telephone communication to H. Gadberry, July 30.

Nemerow, N. L., and R. Armstrong. 1967. Prototype Studies of Combined Treatment of Wastes from 22 Tanneries and Two Municipalities. Purdue University, Engineering Bulletin, Extension Series No. 129 (Part 2). pp. 593-601.

National Institute for Occupational Safety and Health (NIOSH). 1980a. Special Occupational Hazard Review for Benzidine-Based Dyes. U.S. Department of Health, Education, and Welfare. Washington, D.C.

National Institute For Occupational Safety and Health (NIOSH) 1980b. Technical Report: The Carcinogenicity and Metabolism of Azo Dyes, Especially Those Derived from Benzidine. U.S. Department of Health, Education and Welfare, Washington, D.C.

Patton, T. C. 1973. Pigment Handbook, Vol. I and II. Wiley Interscience Publishers, New York, New York.

Peters, E. 1979. McGrew Color Graphics, Kansas City, Missouri. Personal communication to H. Gadberry. June 8.

Powell R., et al., 1979. Survey of the Manufacture, Import, and Uses for Benzidine, Related Substances, and Related Dyes and Pigments. EPA-560/13-79-005, EPA, Washington, D.C. 212 pp.

Radding, S. B. et al. 1978. Assessment of Potential Toxic Releases from Leather Industry Dyeing Operations. EPA 600/2-78-315. EPA, Cincinnati, Ohio. 64 pp.

Renson, J. 1979. National Association of Printing Ink Manufacturers. Harrison, New York. Telephone communication to H. Gadberry, July 10, and letter to H. Gadberry, July 17.

Research Triangle Institute (RTI). 1979. Final Report Prioritization of Emissions from Textile Manufacturing Operations on the Basis of Potential Impact of New Source Performance Standards. EPA, Contract No. 68-02-2612-64, April.

Richardson, R. 1979. E. I. DuPont de Nemours, Inc., Wilmington, Delaware. Telephone communication to H. Gadberry, June 22.

Rubber World. 1979. U.S. and World Rubber News. Rubber World, Vol. 199, No. 5, February 1979. p. 18.

Schafer, B., and W. Bastin. 1979. Smith-Grieves Printing Company, Kansas City, Missouri. Personal communication to H. Gadberry, July 6.

Sheldrick, J. E. 1979. Battelle, Columbus, Ohio. Personal communication to F. Hoffmeister. August.

Skeist, I. 1962. Handbook of Adhesives. Van Nostrand Reinhold Company, New York, New York.

Snell, Foster D., Inc. 1978. Assessment of Industrial Hazardous Waste Practices, Rubber and Plastics Industry: Rubber Products Industry, EPA-530-SW-163C.3. EPA, Washington, D.C. March.

Society of the Plastics Industry, Inc. (SPI). 1979. Facts and Figures of the Plastics Industry. 1979 Edition. SPI, 355 Lexington Avenue, New York, New York 10017. p. 34.

Statistical Policy Division. 1972. Standard Industrial Classification Manual, 1972. Executive Office of the President, Office of Management and Budget, Government Printing Office, Washington, D.C.

Sutt, K. 1979. Sinclair and Valentine Ink Company, Kansas City, Missouri. Personal communication to H. Gadberry. June 8.

Sverdrup and Parcel and Associates, Inc. 1978. Technical Study Report BATEA-NSPS-PSES-PSNS. Textile Mills Point Source Category. Contract Nos. 68-01-3289, 68-01-3884. EPA, Washington, D.C. November.

Tanner's Council of America (TCA). 1977. Directory of Leather Tanner's and Suppliers to the Tanning Industry. 11th ed., New York, New York. 61 pp.

Taylor, J. K. 1979. Waste Research and Reclamation Company, Inc. EauClair, Wisconsin. Telephone communication to H. Gadberry. June 29.

U.S. Department of Agriculture. 1979. Livestock and Meat Situation. LMS-226. Economics, Statistics, and Cooperatives Services, Washington, D.C. April.

Vanderhoff, J. W. 1979. National Printing Ink Research Institute, Philadelphia, Pennsylvania. Telephone communication to H. Gadberry. June 19.

Vathako, G. 1979. International Printing Ink Division of Inmont Corporation, Kansas City, Missouri. Telephone communication to H. Gadberry. June 11.

Versar, Inc. 1976. Assessment of Industrial Waste Practices, Textiles Industry. PB-258 953. EPA, Washington, D.C. June 1976.

Vogt, C. 1974. Development Document for Effluent Limitations Guidelines and New Source Performance Standards for the Unbleached Kraft and Semichemical Pulp Segment of the Pulp, Paper, and Paperboard Mills Point Source Category. EPA 440/1-74-025-a. EPA, Washington, D.C. May. p. 21.

Walanski, K. 1979. Environmental Engineer, DeSoto Coatings, Inc. Des Plains, Illinois. Telephone communication to H. Gadberry and letter to H. Gadberry. July 26.

Welch, W. 1979. Gravure Research Institute, Port Washington, New York. Telephone communication to H. Gadberry. June 7.

Wolthuis, R. J. 1979. Bofors Lakeway Inc., Muskegon, Michigan. Telephone conversation and letter to T. W. Lapp, August 10.

APPENDIX A

REPORT REVIEWERS

The following companies, organizations, and trade associations were provided draft copies of this report for their review and comments.

Al Schneid
Inmont Corporation
150 Wagaraw Road
Hawthorne, NJ 07506

Frank Vincent
American Can Co.
1915 Marathon Ave.
Neenah, WI 54956

John L. Waldo
Saugatuck Dye & Chemical
P.O. Box 97
Saugatuck Station
West Port, CT 06880

Dr. Barry Bochner
Atlantic Chemical Corporation
10 Kingsland Road
Nutley, NJ 07110

Dr. Roderick H. Horning
Crompton & Knowles Corporation
Dyes and Chemicals Division
500 Pear Street
Reading, PA 19603

Gilbert Bassett
Graphic Arts Technical
Foundation
4615 Forbes Street
Pittsburgh, PA 15213

Mr. Frank T. Ryan
Rubber Manufacturers
Association, Inc.
1901 Pennsylvania Avenue, NW
Washington, DC 20006

Dr. Robert M. Lollar
Tanners' Council of America 14
University of Cincinnati
Cincinnati, OH 45221

James E. Renson
National Association of
Printing Ink Manufacturers
500 Manaroneck Avenue
Harrison, NY 10528

Donald L. Morgan
Cleary, Gottlieb, Steen & Hamilton
1250 Connecticut Avenue, NW
Washington, DC 20036

Ralph Harding
Society of the Plastics
Industries, Inc.
1101 17th Street, NW
Washington, DC 20036

Dr. Harshad Vyas
Mobay Chemical Corporation
Verona Dyestuff Division
P.O. Box 385
Union Metropolitan Park
Union, NJ 07083

Dr. P.S. Stensby
Ciba-Geigy Corporation
Dyestuffs & Chemicals Division
P.O. Box 11422
Greensboro, NC 27409

Dr. Hugh Smith
Sun Chemical Corporation
Pigments Division
4526 Chickering Avenue
Cincinnati, OH 45232

Mr. Raymond J. Connor
National Paint and Coatings
Association, Inc.
1500 Rhode Island Avenue, NW
Washington, DC 20005

Dr. John Festa
American Paper Institute
1619 Massachusetts Avenue, NW
Washington, DC 20036

Mr. John Tritsch
American Textile Manufacturers
Institute, Inc.
1101 Connecticut Avenue, NW
Washington, DC 20036

Richard Alsager
BASF Wyandotte Corporation
Pigments Division
491 Columbia Avenue
Holland, MI 49423

APPENDIX B

SAMPLE CALCULATIONS

SAMPLE CALCULATIONS

The following procedures and sample calculations are provided for Tables 3-5 (p. 3-26), 3-7 (p. 3-29), 7-4 (p. 7-15), 7-5 (p 7-16), and 7-6 (p. 7-18).

I. Table 3-5, p. 3-26

Procedure and Sample Calculation

A. From p. 3-5:

Process Losses = ~ 0.25 to 1.0% (based on BAMB raw material).
By-Products = 5 to 15%; 85 to 95% active dye (based on BAMB raw material).
Filtration Losses = 1 to 3% (based on BAB dye)
Drying, Grinding, Standardization, and Packaging = 1 to 5% (based on BAB dye).

B. From Table 3-6: (p. 3-27)

Product Yield = 84% (based on BAMB raw material).
Active Dye Content of Presscake (Footnote b) = 85 to 90% (85% used in all calculation).

C. Convert process losses from a BAMB raw material basis to an active dye basis.

From (A): (Total percent process loss)(Percent active dye from production process)
Lower Percentage: (0.25%)(0.85) = 0.21%
Upper Percentage: (1.0%)(0.95) = 0.95%

The process losses stated in (A) are now 0.21 to 0.95% based on BAB dye.

D. Sample calculations for benzidine-based dyes in 1975 are as follows:

Estimated total U.S. production = 3,800,000 to 4,600,000 pounds (Table 3-4, p. 3-24)
Benzidine-based dye presscake content of standardized dye is 60% (Table 3-6, p. 3-27)

Estimated Loss = (Production rate)(product yield factor)(loss factor)(fractional presscake content of standardized dye)(fractional active dye content of presscake).

$$\text{Loss factor} = \frac{\%\ \text{loss}}{100}$$

1. Processing losses

$$\text{Estimated loss} = (3{,}800{,}000)\left(\frac{1}{0.84}\right)(0.0021)(0.6)(0.85)$$
(lower limit) = 4,845 lb

$$\text{Estimated loss} = (4{,}600{,}000)\left(\frac{1}{0.84}\right)(0.0095)(0.6)(0.85)$$
(upper limit) = 26,532 lb

2. Filtration losses

$$\text{Estimated loss} = (3{,}800{,}000)\left(\frac{1}{0.84}\right)(0.01)(0.6)(0.85)$$
(lower limit) = 23,071 lb

$$\text{Estimated loss} = (4{,}600{,}000)\left(\frac{1}{0.84}\right)(0.03)(0.6)(0.85)$$
(upper limit) = 83,786 lb

II. Table 3-7, p. 3-29

Procedure and Sample Calculations

A. Assumed Product Yield = 84% (see Table 3-6, p. 3-27).

B. 1. Process Vent Loss = 0.1%, either as unreacted starting material or as decomposition products (p. 3-5).
Assume 1 to 10% of the total net losses are unreacted BAMB raw material.
Thus, process vent loss of unreacted BAMB raw material is 0.001 to 0.01%.

2. Processing Loss = 0.25 to 1.0% of the BAMB-based material (p. 3-5).
Assume that 1% of this loss is unreacted BAMB raw material.
Thus, processing losses are 0.0025 to 0.01% as unreacted BAMB raw material.

3. Filtration Losses: Assume 1 to 10 lb of filtrate per pound of standardized dye and a filtrate content of 0.5 ppm of unreacted BAMB raw material (p. 3-5).

4. Drying, grinding, standardization, and packaging losses: Assume an unreacted BAMB raw material content of 20 ppm in each pound of filter presscake for each BAB dye (p. 3-6).

5. Product losses: Assume an unreacted BAMB raw material content of 5 to 10 ppm in each pound of standardized dye (p. 3-6).

C. Sample calculation for benzidine-based dyes in 1975 are as follows:

Estimated total U.S. production = 3,800,000 to 4,600,000 pounds (Table 3-4, p. 3-24).
Molecular weight of benzidine = 184.2.
Average molecular weight of benzidine-based dyes = 800 (Table 3-6, p. 3-27).
Estimated loss = (Production rate)(product yield factor)(fractional presscake content of standardized dye)(fractional actual dye content of presscake)$(\frac{\text{benzidine mol. wt.}}{\text{average dye mol. wt.}})$
Fractional presscake content of standardized dye = 0.60 (Table 3-6, p. 3-27).
Fractional active dye content of presscake = 0.85 (Table 3-6, p. 3-27).

1. Vent losses (lower limit):

$$\text{Estimated loss} = (3{,}800{,}000)(\frac{1}{0.84})(0.00001)(0.6)(0.85)(\frac{184.2}{800}) = 5\text{ lb}$$

2. Processing losses (lower limit):

$$\text{Estimated loss} = (3{,}800{,}000)(\frac{1}{0.84})(0.000025)(0.6)(0.85)(\frac{184.2}{800}) = 13\text{ lb}$$

3. Filtration losses (lower limit):

Estimated loss = (Production rate)(filtrate weight)(level of raw material in filtrate)
$= (3{,}800{,}000)(1)(0.5 \times 10^{-6}) = 2$ lb

4. Drying, grinding, standardization, and packaging losses (lower limit):

Estimated loss = (Production rate)(fractional presscake content of standardized dye)(level of raw material in presscake)
$= (3{,}800{,}000)(0.6)(20 \times 10^{-6}) = 46$ lb

5. Product loss (lower limit):

Estimated loss = (Production rate)(level of raw material in standardized dye)
$= (3{,}800{,}000)(5 \times 10^{-6}) = 19$ lb

III. Table 7-4, p. 7-15 and Table 7-5, p. 7-16.

Procedure and Sample Calculation

3,3'-dichlorobenzidine in 1975

A. From Table 7-6: Total loss range of DCB-based pigment due to transfer and handling is 91,000 to 274,000 lb.

B. From Table 7-3: Calculate the range of percent contribution of each DCB-based pigment to the total production figures.

Examples

Yellow 12 $(\frac{6028000}{9666000})(100) = 62.4\%$; $(\frac{6028000}{9781000})(100) = 61.6\%$

Yellow 14 $(\frac{1840000}{9666000})(100) = 19.0\%$; $(\frac{1840000}{9781000})(100) = 18.8\%$

C. Multiply the percentage range for each DCB-based pigment (from B) and the estimated losses of DCB-based pigment (from A). This prorates the losses according to production volumes. Add losses to annual production figures in Table 7-3.

Example

Yellow 12 (91,000)(0.616) = 56,000 lb (lower estimate)
(274,000)(0.624) = 171,000 lb (higher estimate)

Estimated total Yellow 12 production = 6,028,000 + 56,000 = 6,084,000 lb (low)
6,028,000 + 171,000 = 6,199,000 lb (high)

Repeat this procedure for all DCB-based pigments.

D. Calculate the quantity of free amine required for the total production of each DCB-based pigment. The molecular weight of DCB = 253.2; DMOB = 244.3; and DMB = 212.3. Pigment molecular weights are given in Table 7-1.

Example Yellow 12 $\frac{253.2}{629.4} = 0.402$

(0.402)(6,084,000) = 2,446,000 lb (low estimate)
(0.402)(6,199,000) = 2,492,000 lb (high estimate)

The calculated range of DCB required to produce Yellow 12 in 1975 was 2,446,000 to 2,492,000 lb.

E. Repeat this procedure for each DCB-based pigment. Sum the weights of DCB required for each pigment to obtain the total DCB requirement of 1975. This sum is estimated to be 3,797,000 to 3,907,000 lb.

F. Use the total DCB requirement obtained in (E) to calculate the estimated losses in Tables 7-4 and 7-5.

For Table 7-4: Purification losses = 0.5 to 1.0%

$$1.000 - 0.005 = 0.995$$
$$1.00 - 0.01 = 0.99$$

In 1975: $\frac{3,797,000}{0.995} = 3,816,000$ lb; $\frac{3,907,000}{0.99} = 3,946,000$ lb

Therefore purification losses are:

(3,816,000) - (3,797,000) = 19,000 lb
(3,946,000) - (3,907,000) = 39,000 lb

G. Use same procedure as shown in (F) to calculate purification losses and filtration losses in Table 7-4 and the optional tetrazonium filtration losses and pigment formation losses in Table 7-5.

IV. Table 7-6, p. 7-18

Procedure and Sample Calculation

3,3'-dichlorobenzidine-based pigments in 1975

A. From Table 7-3: Total production range of DCB-based pigments in 1975 was 9,666,000 lb to 9,781,000 lb.

Of this total quantity, Yellow 12 production was 6,028,000 lb and all of the other DCB-based pigments were 3,638,000 to 3,753,000 lb.

B. Data on p. 7-17 provides percent distribution of DCB-based pigments between the three processing forms. Calculate distribution using total production figures in (A).

Yellow 12:
Dry toner (0.273)(6,028,000) = 1,646,000 lb
Flushed color (0.704)(6,028,000) = 4,244,000 lb
Presscake and dispersions (0.023)(6,028,000 = 139,000 lb

All other DCB-based pigments:
Dry toner (0.53)(3,638,000) = 1,928,000 lb
(0.53)(3,753,000) = 1,989,000 lb

Flushed color (0.141)(3,638,000) = 513,000 lb
(0.141)(3,753,000) = 529,000 lb

Presscake and dispersions (0.329)(3,638,000) = 1,197,000 lb
(0.329)(3,753,000) = 1,235,000 lb

Total DCB-based pigments as:	Dry toner	3,574,000 to 3,635,000 lb
	Flushed color	4,757,000 to 4,773,000 lb
	Presscake and dispersions	1,336,000 to 1,374,000 lb

C. Loss ranges are presented in Table 7-6 for each processing form (i.e., dry toner, flushed color, and presscake).

Apply these loss ranges to totals for each processing form derived in (B).

Example - Dry toner: loss range = 1 to 3%
total production = 3,574,000 to 3,635,000 lb (from B)

The total quantity of DCB-based pigment processed as dry toner before any transfer and handling losses are as follows:

$$\frac{3,574,000}{0.99} = 3,610,000 \text{ lb (lower limit)}$$

$$\frac{3,635,000}{0.97} = 3,747,000 \text{ lb (upper limit)}$$

Losses due to transfer and handling are:

$$(3,610,000) - (3,574,000) = 36,000 \text{ lb (lower limit)}$$

$$(3,747,000) - (3,635,000) = 112,000 \text{ lb (upper limit)}$$

D. Use same procedure in (C) to calculate other losses in Table 7-6.